# MIDDLE DISTILLATE FUELS FROM FISCHER-TROPSCH WAX USING ANION-MODIFIED ZIRCONIA CATALYSTS

by

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MIDDLE DISTILLATE FUELS FROM FISCHER-TROPSCH WAX USING ANION-MODIFIED ZIRCONIA CATALYSTS

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Platinum-promoted anion-modified zirconia catalysts, such as tungstate-modified zirconia and sulfate-modified zirconia were studied in the hydrocracking and hydroisomerization of long-chain alkanes in Fischer-Tropsch waxes for producing high yields of middle distillates ($C_{10}$-$C_{20}$) transportation fuels.

Model compounds such as n-$C_{24}$ and n-$C_{36}$ were used as reactants and the reactions were carried out in a microautoclave reactor system. To compare the catalytic performances of various catalysts, a set of particular reaction conditions, such as 200°C, 300-psi initial hydrogen pressure, 25-minute reaction time and 4:1(wt) reactant to catalyst ratio were applied. For catalyst samples with platinum (Pt), the Pt concentration was chosen as 0.5 wt%.

In the conversion of long-chain normal paraffins, Pt-promoted tungstated zirconia (PtWZr) has a high selectivity to hydroisomerization and Pt-promoted sulfated zirconia (PtSZr) is a very strong cracking catalyst. Either PtWZr or PtSZr alone gives a low yield of middle distillate products. It is found that a hybrid catalyst system consisting of PtWZr and SZr effectively combines the functions of the two components and leads to increased yields of middle distillates under the same reaction conditions. The increased reactivity and selectivity to middle distillates of PtWZr/SZr suggests active beneficial interactions between the components. The

performance of PtWZr/SZr hybrid catalysts is affected by the component ratio. For a given reaction condition, there is an optimum component ratio for a maximum yield of middle distillates. Hydrogen pressure is an important factor affecting the reactivities and selectivities of the two types of anion-modified zirconia catalysts. Higher yields of middle distillates are obtained from n-$C_{36}$ with PtWZr/SZr catalysts at 300-psi hydrogen pressure than are obtained at 100-psi hydrogen pressure.

PtWZr/zeolite hybrid catalysts were also prepared and tested in the conversion of n-$C_{36}$. Mordenite, Y zeolite and Beta zeolite with similar Si/Al ratios were used as the second component. The hybrid catalysts have a higher reactivity in the production of middle distillates than the individual components.

Characterization tests, such as SEM, EDX, XRD, TPD, BET and CO chemisorption showed that the hybrid catalysts prepared in this research are physical combination of their components.

This research demonstrated a novel approach of using hybrid anion-modified zirconia catalysts for producing middle distillate fuels. The work furnishes a valuable foundation for further investigations.

## DESCRIPTORS

Anion-modified zirconia

Catalyst preparation

Fischer-Tropsch wax

Hybrid catalyst

Hydrocracking

Hydroisomerization

Impregnation

Long-chain normal paraffin

Middle distillates

Solid acid catalyst

Sulfated zirconia

Transportation fuels

Tungstated zirconia

Zeolite

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# 1.0 INTRODUCTION

The Fischer-Tropsch (FT) synthesis, which converts CO and $H_2$ to a range of hydrocarbons, is inherently a very good way to produce high quality, environmentally clean transportation fuels, especially middle distillate liquids used as jet and diesel fuels. Since premium fuel products can be produced with the FT process, they can be used as blending agents to upgrade traditional transportation fuels made from petroleum. The cetane number of an FT diesel is as high as 70-75, which is much higher than the market requirement of 45. [(1)] The high cetane number of FT diesel helps to reduce particulate emissions from diesel engines.

The FT synthesis process uses synthesis gas, which contains mainly CO and $H_2$, as the raw material. The synthesis gas is converted to hydrocarbon products utilizing a number of gas-to-liquid (GTL) technologies with cobalt or iron as the catalyst. Although it is cheaper to obtain synthesis gas from natural gas, which is mainly methane, any carbonaceous substances can be a source of synthesis gas. For coal-rich countries such as the United States, China and South Africa, the FT process can be a vital solution. In the US, there is about thirty times as much energy in coal as in natural gas.

While natural gas supplies are expected to remain tight for years to come in many places, there are huge amounts of so-called stranded natural gas fields in some mid-East countries and in Alaska. No pipelines are available for the stranded natural gas to be exported economically. FT plants can be built in those areas to convert natural gas to FT products, which can then be

transported to other places. Several companies, which have built pilot plants in the US to convert natural gas to diesel and jet fuels, are planning to build commercial units in mid-East countries such as Qatar. Shell has built a plant in Malaysia to utilize its plentiful natural gas resources to produce high quality diesel fuel using the FT process. [2] If the stranded natural gas cannot be converted and stored, it has to be flared and would release a large amount of $CO_2$ from the burning methane. $CO_2$ is a greenhouse gas that is a growing environmental problem. The FT process converts stranded natural gas for effective storage and delivery as well as helping to reduce the release of greenhouse gases.

Because of the sequential chain-growth mechanism involved in FT reactions, it is not possible to obtain paraffin fractions with a specific carbon-chain range.[2, 3] FT products are always mixtures of light and heavy hydrocarbons and some oxygenates, which includes light gases, naphtha and jet and diesel fuel fractions. The distribution of FT product chain length as a function of the chain-growth probability ($\alpha$) is described by the Anderson-Schulz-Flory (ASF) equation (Figure 1) [2]. A commercial FT process for producing diesel fuels operates with a high $\alpha$ value, which produces a large amount of high molecular weight hydrocarbons, termed FT waxes. These FT waxes must be cracked and isomerized to obtain the desired transportation fuels.

The FT synthesis as practiced by Sasol in South Africa and by Shell in Malaysia uses proprietary catalysts to convert FT waxes to the desired fuel fractions such as diesel fuels. Sasol also started to obtain diesel fuel of high quality from hydrocracking and hydroisomerization of FT waxes. [1, 4] It is generally recognized that the catalysts used in FT wax cracking and isomerization should contain a metal, such as Pt, on a support, such as amorphous silica-alumina or zeolites. [4] The silica-alumina or zeolite-based catalysts usually have low reactivities and need

high reaction temperatures, about 350-500 °C, to obtain acceptable conversions.[5-18] In the present work, we aim at obtaining a readily available, active catalyst system which can be configured to convert FT waxes into clean high octane gasoline, high cetane diesel or jet fuel under mild conditions. The catalyst systems we have studied are based on anion-modified zirconia catalysts which have demonstrated high reactivities in the conversion of long-chain paraffins in FT waxes.

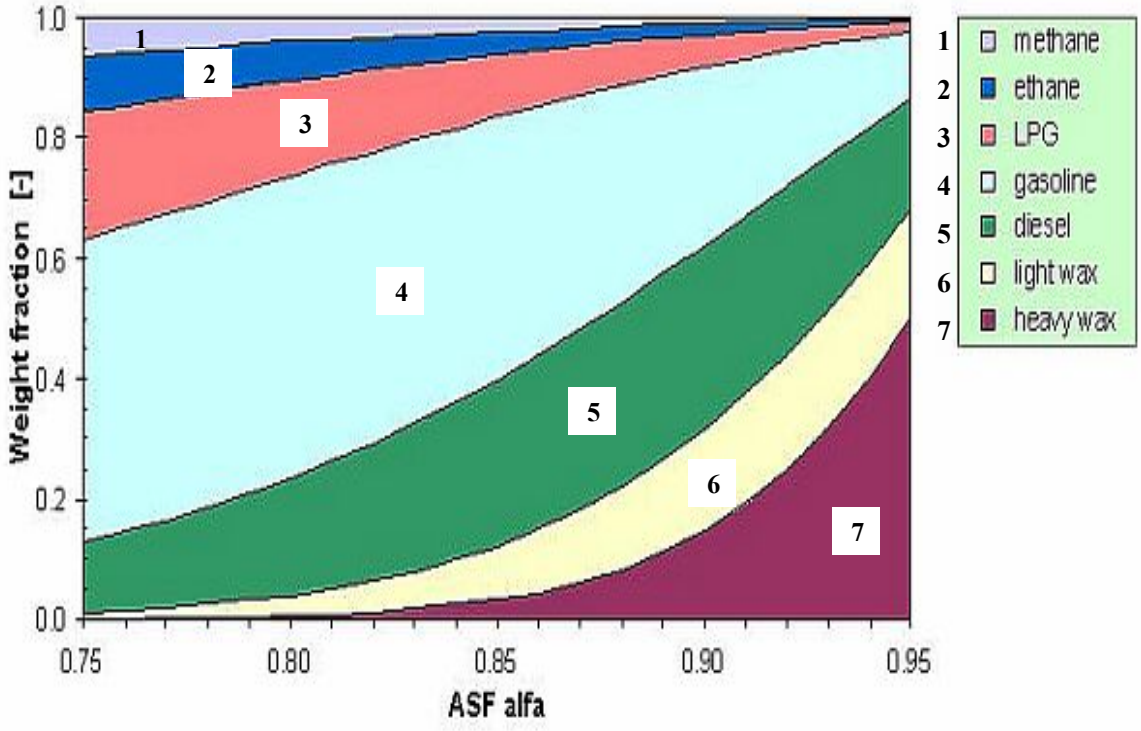



**Figure 1. Fischer-Tropsch Product Distribution**

The initial publication on the extraordinary catalytic activity of an anion-modified zirconia, i.e. sulfated zirconia, was in the early 1960s [19]. Hino and Arata [20] found that so-called superacidity was generated on zirconia by treatment with sulfuric acid. The catalyst was effective

in isomerizing n-butane to isobutane at room temperature. There is still no conclusive explanation for the extraordinary reactivity of the anion-modified zirconia, which is often considered as a strong solid acid. Postulated structures of sulfated zirconia are shown in Figure 2. The acidity of sulfated zirconia (SZr) catalysts was attributed to the electron-withdrawing function of the $SO_4^{2-}$ group that leads to an electron-deficiency of the zirconium atoms.

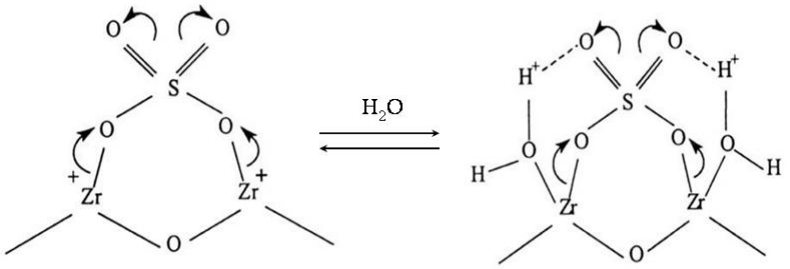



**Figure 2. Acid Structures of Sulfated Zirconia**

G. N. Lewis generalized the acid concept to non-protonic systems and defined an acid as a substance that can accept electrons. [21] The electron-deficient zirconium centers behave as Lewis acid sites, which can change to protonic Bronsted acid sites by addition of water molecules. Later, it was found that acid sites with similar properties can also be generated by supporting tungstate, $WO_3$, on zirconia.[22-31]

Anion-modified zirconia catalysts, especially sulfated zirconia, have attracted extensive interest. However, questions remain about the nature of their catalytic activities. [30, 32, 33] It is now generally accepted that these zirconia catalysts are weaker acids than they were thought to be. In addition to inadequate methods for measuring the acid strengths of these solid catalysts, the mechanisms present in the isomerization and cracking of paraffins are far from clear.

Although acidity plays an important role in catalyzing these reactions, many other functions have been proposed to explain their activity. In addition to the fairly well-known activity of traditional Lewis or Bronsted acids, the high catalytic activity of sulfated zirconia may also result from its activity as an oxidation agent for hydrocarbons.[34, 35] Farcasiu and co-workers studied the reaction of sulfated zirconia in the presence of adamantane and concluded that the reaction involves oxidation followed by hydride transfer. The oxidizing ability of the sulfate group was greatly increased when combined with zirconia support. [34]

The roles of metal promoters and hydrogen spillover are also issues under investigation and debate.[36-42] It is generally known that a noble metal promoter activates hydrogen and keeps the active sites from deactivation by coke formation.[43-48] But some other functions of metal promoters should also be considered. Ebitani et al.[49]claimed that the metal increased the concentration of Bronsted acid sites by hydrogen spillover. Demirci et al. [50] postulated that a metal-proton adduct is the active site. Santiesteban et al.[51] proposed a strong interaction between metal and support in studying pentane isomerization with Pt-promoted tungstated zirconia. They claimed that Pt facilitated the reduction of tungsten and probably enhances hydrogen spillover. Through strong interaction with tungstated zirconia, Pt could lower the acid activity of the catalyst. [51]

Sulfated and tungstated zirconias have been studied for the isomerization of normal paraffins. [26, 37, 52-55] Most of the studies were carried out on the isomerization of short-chain hydrocarbons, such as n-butane, n-pentane and n-hexane[37, 54, 56], which has important application in the octane-number improvement processes used in the manufacture of gasoline. Hosoi et al. used naphtha as feedstock and reported that the activity and stability of sulfated zirconia were greatly improved by loading a small amount of Pt (0.5 wt %). [57] It has been found

that the isomerization and cracking of heptane and heavier paraffins differ from the lighter paraffins. [24, 52] Not all of the experience obtained with experiments with light paraffins is applicable to heavy paraffins. For example, it appears that the hydrocracking of paraffins heavier than heptane over Pt-promoted sulfated and tungstated zirconia may not proceed via the conventional bifunctional mechanism involving initial dehydrogenation to an olefinic intermediate. Experiments have shown that addition of olefins (from 10 ppm to 50 wt%) is detrimental to paraffin conversions, behavior not expected via a bifunctional route.[58, 59] To study the conversion of long-chain paraffins in the FT wax, we used longer paraffins, such as n-$C_{24}$ and n-$C_{36}$, as the model compounds in our research. Very little work has been reported with such long-chain reactants.

Paraffins with longer chains crack more easily than those with short chains. [24] For the production of transportation fuels, cracking of the FT long-chain paraffins (waxes) should be limited to obtain middle distillate fuels. Extensive cracking leads to light products that are not in the desired ranges. It has been found that sulfated zirconia is a very reactive cracking catalyst. [29, 43, 52, 54, 58, 60, 61] When sulfated zirconia catalysts were used with longer chain paraffins, such as normal hexadecane (*n*-$C_{16}$), they readily converted the reactant into light products with carbon number less than seven. Compared to sulfated zirconia, tungstated zirconia is a milder cracking catalyst for long-chain hydrocarbons. This can be explained by the higher hydrogen transfer rates over the surface of tungstated zirconia. [26] With a shorter lifetime of the adsorbed carbenium ions, products leave the surface of tungstated zirconia before further cracking occurs. Iglesia et al. [26, 52] and Zhang et al. [53] have reported that Pt-promoted tungstated zirconia is more stable than sulfated zirconia and has higher selectivity to isomerization products from n-hexadecane.

While sulfated zirconia and tungstated zirconia have been studied individually for years, there is no reported study on combining the functions of these two anion-modified zirconia catalysts for converting long-chain hydrocarbons. The present research explores the possibility of combining the catalytic features of these two types of zirconia catalysts for an appropriate balance of hydroisomerization and hydrocracking functions that would lead to higher yields of desirable fuel products. Our work is aimed at obtaining middle distillate transportation fuels, such as jet and diesel, from long-chain paraffins in FT waxes. We prepared, tested and characterized various combinations of Pt-promoted tungstated zirconia with sulfated zirconia or with zeolites, which we termed "hybrid" catalysts.

In the application of hybrid catalysts, studies on mixtures of catalysts have been reported. Catalysts consisting of mechanical combinations of Pt-promoted oxides ($Al_2O_3$ or $SiO_2$) and an acidic component (zeolite or sulfated zirconia) in the hydroisomerization of normal paraffins have been reported.[39, 41, 62-66] Hybrid catalysts composed of $Pt/SiO_2$ and ZSM-5 zeolite have been studied for the isomerization of n-pentane and n-octane at 250°C.[39, 63, 65] The hybrid catalyst showed an improved activity and selectivity as compared to Pt/ZSM-5 or to $Pt/SiO_2$. Hybrid catalysts consisting of $Pt/Al_2O_3$ (or zeolite) and sulfated zirconia were reported to have enhanced activity in the hydroisomerization of n-hexane, n-octane and n-tetradecane at 220-360°C to give isomers of the reactants.[41, 62, 64] Enhancement of the activity and selectivity of the composite catalysts, as compared to individual components, was rationalized in terms of spillover of hydrogen and transfer of some reaction intermediates from the surface of the sulfated zirconia to that of the zeolite. [62, 64]

The reaction conditions under which catalytic reactions take place are critical in determining activity and product distribution. In addition to reaction temperature and reaction

time, the pressure of hydrogen is an important factor in affecting the performances of many catalysts. Some work on the effect of hydrogen on solid acid cracking and isomerization abilities has been reported. [26, 36, 39, 41, 51, 67-70] Shishido et al. observed the promotional effects of hydrogen on the catalytic activity for cumene cracking and proposed that protonic acid sites could be formed by molecular hydrogen.[67] Zhang and co-workers considered the effect of spillover hydrogen to be important in the regeneration of Bronsted acid sites and in the stabilization of carbenium ion intermediates.[39] Calemma et al. found that the hydrogen pressure affected the behavior of catalysts more significantly when working with paraffins heavier than *n*-hexadecane.[5]

The principal objective of this dissertation is to study the use of Pt-promoted anion-modified zirconia catalysts in the conversion of the long-chain paraffins in FT waxes into transportation fuels. The main emphasis is on obtaining middle distillates, such as diesel fuels. We investigated hybrid catalyst systems as a new approach to change the reactivity and product distribution. By combining Pt-tungstated zirconia (PtWZr) with sulfated zirconia or with various zeolites, increased yields of middle distillate fuel products were obtained. Besides component ratio, hydrogen pressure was also found to be a key factor that affects the product distributions with the two anion-modified zirconias and their hybrid catalysts. Hybrid catalysts consisting of PtWZr and zeolite components were also found to give increased yield of middle distillates. A number of catalyst characterization tests were carried out to obtain a better understanding of the nature of the catalysts and their performance. Evidence has been obtained that the hybrid catalysts are physical mixtures of their components.

To compare the performances of various catalyst systems, the catalytic reactions were carried out at fixed reaction conditions, such as 200°C, amount of catalyst and reactant for each

run and reaction time. The encouraging and promising results from our exploratory research with hybrid catalysts have laid a foundation for further investigations. The hybrid catalysts are flexible for different desired products and have high potential in increasing the yield under optimum conditions. Other reaction conditions, different preparation methods, various catalyst components and reactants should be tested to further understand and apply the novel hybrid catalysts in the conversion of FT waxes. We hope that the catalysts studied in this research will lead to their eventual commercial use.

# 2.0 BACKGROUND

## 2.1 ACIDITY AND ACTIVITY OF SOLID ACIDS IN HYDROCARBON CONVERSION

Anion-modified zirconias, such as sulfated and tungstated zirconia, are solid acid catalysts whose catalytic activity for the isomerization and cracking of hydrocarbons has been attributed to their being superacids. [20, 22, 71, 72] Other researchers [30] [32] [33] have questioned whether these materials are really superacids. We believe that, although their acidities play an important role in hydrocarbon conversions, the zirconia catalysts may not be "superacids". Their reactivity can be related to other functions as well.

### 2.1.1 Superacidity and Solid Acid Catalysts

Since the early 1960s, superacids, such as magic acid ($HSO_3F$: $SbF_5$), are known to react with saturated hydrocarbons even at low temperatures. [21, 73] This discovery initiated extensive studies on hydrocarbon conversions catalyzed by strong acids. An arbitrary but widely accepted definition of superacids was proposed by Gillespie. [74, 75] He defined superacids as any acid system that is stronger than 100% sulfuric acid. The Hammett acidity function, Ho, [76] measures acidity by the degree of protonation of weakly basic indicators in a solution.

The Hammett function, as showed in equation 1, expresses the acid strength when an organic base, B, reacts with a Bronsted acid to form the conjugate acid, BH+, and changes its color.

$$Ho = pK_{BH+} - \log [BH+]/[B] \qquad (1)$$

[B] is the concentration of the neutral base (indicator) that reacts with a Bronsted acid (AH); [BH+] is the concentration of the formed conjugated acid.

The Ho value of 100% sulfuric acid is -12. Therefore, a superacid is defined as an acid system that has a Ho value less than -12. For example, fluorosulfuric acid ($HSO_3F$) has a Ho value of about -15.1 and qualifies as a superacid.

Because of their reactivities in converting paraffins, acid catalysts play a vital role in the petroleum industry where they are widely used in various cracking and isomerization reactions to process oils and oil products. The strong liquid acids have corrosion and recovery problems in practical applications; solid acid catalysts do not have these disadvantages and are better choices for industrial processes. Different types of solid acids have been developed and studied for acid-catalyzed hydrocarbon reactions. Hino and Arata [20, 22, 71, 72] pioneered the investigation of anion-modified zirconia catalysts after the catalytic activity of sulfated zirconia was observed in the 1960s.[19] In 1979, they published their first paper in this field [20]finding that strong acidity was generated on zirconia, $ZrO_2$, by treatment with sulfuric acid. The sulfate-modified zirconia, $SO_4^{2-}/ZrO_2$, was effective in catalyzing normal butane isomerization to isobutane at room temperature - a reaction that does not take place even with 100% sulfuric acid. See Figure 2. It was later found that the acidic structures can also be generated by supporting tungstate, $WO_3$, on zirconia.[71]

Reaction rate measurements are direct ways to measure the activity of a solid catalyst. A close relationship between activity and acidity has been found for liquid acids as well as for solid acids. Since n-butane isomerization is a reaction supposedly catalyzed by superacid catalysts, it was quite natural to relate the extraordinary catalytic reactivity of sulfated zirconia with its acid strength. [20, 71, 77-81] These researchers used the Hammett function and temperature-programmed desorption (TPD) to determine that the acid strength of sulfated zirconia was in the range of -16.1 to -19, suggesting superacidity. However, as discussed below, limitations of acidity measurements on solid acids, especially the drawbacks of the Hammett function have been pointed out. [21, 30, 82, 83]

### 2.1.2 Doubts about Superacidity

Gillespie's definition of superacids relates to Bronsted acid systems. While the Bronsted acid-base interaction always involves a proton transfer reaction that allows meaningful comparison, in the Lewis acid-base interaction there is no such common denominator. [21] The result is that the definition of acid strength has no real meaning with Lewis acids. Solid acids generally have both Bronsted and Lewis acid sites. The use of the Ho function to determine the "superacidity" of heterogeneous solid acids has many obstacles.

To test the acidity, the basic indicator has to be weak enough not to affect the original acidity of the solid acid sample. Over the surface of a solid sample, it is hard to achieve the equilibrium measurement using these indicators. [30, 82] Moreover, the solid acid samples are often colored or dark and cause inaccuracy in visual observations of color changes. The acid sites on a solid surface are of different strengths and the indicators may be adsorbed only to part of the acid sites not distinguishing how they are absorbed. The surface area available for acidity determinations may have widely different acidic properties from the bulk material. It is possible

that only a small part of the detected acidic sites are strong enough in catalysis of paraffin conversions. The generic term of acidity includes both acid strength and surface concentration of the acid sites. It is apparent that a single technique can not provide adequate accurate information on solid acids.

The application of adsorption and desorption of base molecule provides other techniques to measure the acidity of a solid acid {Parrillo, 1994 #427}. The adsorption heat [80] and activation energy from temperature-programmed desorption (TPD) tests [77] have been correlated with acid strength in terms of the Hammett function. However, this method can also lead to inaccurate conclusions. For example, the TPD of adsorbate molecules may involve decomposition species, especially on strong acids that can also be absorbed on both acid and base sites. The base molecules could be absorbed on acid sites that are not catalytically active. The desorbed molecules could diffuse and be reabsorbed on the acid sites [85]. Peters et al. have even shown that a non-acidic solid, such as CaO, can also retain a base, $NH_3$, at high temperatures [86], which points out the uncertainty of the correlation of acid strength with the results of desorption tests.

Hall and Umansky [32] reported that a sulfated zirconia sample did not demonstrate strong superacidity and that its acidity was close to that of a mordenite or a Y-zeolite sample. They also found that the acid strength was more important than the acid concentration for the acidity of solids. Other researchers also found that the acidity of sulfated zirconia was not as high as expected.[27, 49, 82, 87-89]

Since there is a lack of satisfactory methods of determining the acidity of a solid, the superacidity of anion-modified zirconias is in doubt. Because of the complexity of a solid acid catalyst, all the experimental results should be interpreted with caution. In any case, it is important to note that the catalytic properties of solid acid catalysts strongly depend on the

method of preparation, pre-treatment and storage. These differences add to the disagreement of acidity among various researchers. Even if the acidic properties of a solid acid could be accurately determined, it would still be difficult to relate acidity to catalytic reactivity because of the wide distribution of the type and strength of the surface acidic sites and the uncertainty about what sites are catalytically active.

## 2.2 OTHER PROPERTIES OF ANION-MODIFIED ZIRCONIA RELATED TO REACTIVITY

The remarkable catalytic reactivity of anion-modified zirconia catalysts in hydrocarbon conversion suggests that they possess special characteristics. Since the "superacidity" of sulfated zirconia has been subjected to controversy and revision, there must be other special properties that lead to its extraordinary catalytic performance. Although no clear consensus has been reached so far, many theories have been proposed to explain the origin of the reactivity.

Farcasiu et al.[33, 90] proposed that sulfated zirconia mainly functions as an oxidizing agent. They studied the mechanism of adamantane conversion using sulfated zirconia at 65 to 150°C. Adamantanone and 1-adamantanol were observed in the products, showing that the reaction of adamantane and sulfated zirconia was an oxidation process in which sulfated zirconia is the electron acceptor. At 150 °C, part of the sulfate group on the zirconia surface was reduced to sulfide. Their experimental results showed an increase in the oxidizing ability of sulfate when combined with a zirconia support. The high catalytic activity of sulfated zirconia was ascribed to

its exceptional activity as an oxidizing agent for converting hydrocarbons. They believed that the generation of carbenium ions is a reduction-oxidation process.

The catalytic performance of anion-modified zirconia catalysts can be related with their surface structures. Modified by metal oxides, zirconia crystal structure and crystallite size were changed. Zirconia crystallites sinter and become predominately monoclinic after high temperature oxidation (>630°C). However, pure tetragonal zirconia crystallites may be stabilized by impregnation with tungstate before the oxidative treatment. [91] In addition to stabilizing tetragonal zirconia crystallites, tungstate surface species inhibit zirconia sintering, leading to smaller crystallites than in pure zirconia. [52] The tetragonal content in zirconia also depends on the concentration of tungstate at each oxidation temperature. With concentration about 12 wt% W, zirconia crystallites are purely tetragonal. At oxidation temperature higher than 900°C, surface tungstate species agglomerate and become less effective sintering inhibitors. Sulfate species also inhibit the loss of zirconia surface area after oxidative treatment [92]. However, these sulfated species decompose and desorb as $SO_3$ at relatively low oxidation temperature of 600°C which results in rapid zirconia sintering [61]. The thermal stability of tungstated species differs greatly from the poor stability of sulfated species supported on zirconia. When Pt is present, the sulfated species decompose to $H_2S$ even below 600°C in hydrogen.

Barton and co-workers found that the tungstate domain grows and reduction behavior changes as the surface tungstate species increases on zirconia support [52]. Tungstate species convert from strongly bound structures to two- and three-dimensional structures that reduce at lower temperatures. These reducible tungstate domains may act as redox sites required for the formation of $H^+$ species from $H_2$ and paraffins on tungstated zirconia catalysts. The tungstate domains of intermediate size have acid properties that can be related to their ability to form

$W^{6-n}O_x$-(n-$H^+$) Bronsted acid centers under reducing conditions. Maximum hydrogen uptakes were detected on tungstated zirconia samples that show maximum catalytic activity for n-heptane isomerization, suggesting that the formation of these $W^{6-n}O_x$-(n-$H^+$) reduction centers is related to the stabilization of carbenium intermediates.

Generally speaking, sulfated zirconia is a strong hydrocracking catalyst; tungstated zirconia is a weaker acid with higher selectivity to isomerization reactions. Iglesia et al. [25, 26] and Zhang et al. [93] reported that tungstated zirconia is more stable than sulfated zirconia and gives higher selectivity to isomerization products from normal hexadecane (*n*-$C_{16}$). In addition to the difference in their acidity, the different performance of these two catalysts can also be explained by their hydrogen transfer rate on the catalyst surfaces. [52] Higher hydrogen transfer rates on the surface of tungstated zirconia may result in a shorter lifetime of adsorbed carbenium ions, which leave the catalyst surface before further cracking occurs. [26]

## 2.3 HYDROISOMERIZATION AND HYDROCRACKING OF ALKANES USING SOLID ACIDS

Generally, the solid acid catalysts for hydroisomerization and hydrocracking of paraffins are bifunctional, consisting of both metal and acid components. There are many studies devoted to the reaction mechanisms involved in the conversion of paraffins. [94-98] A generally accepted overall series of reaction steps in paraffin conversion is shown in Figure 3.

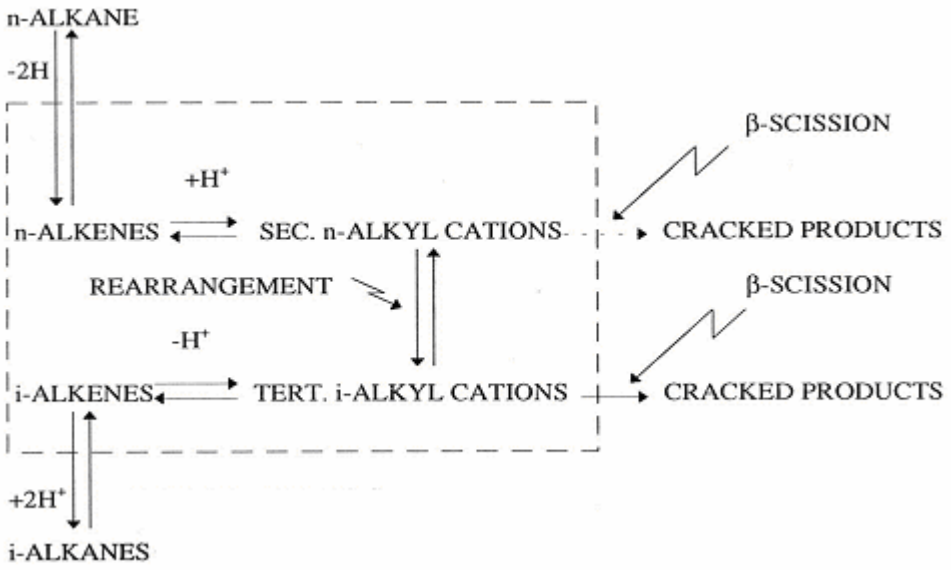



**Figure 3. General Steps of Paraffin Conversions**

Although direct evidence supporting the presence of carbocations, such as carbenium ions, on the surface of a solid catalyst has not yet been provided, it is generally assumed that the formation of carbenium ions is fundamental in hydrocarbon conversion over acid catalysts. [21] On a solid acid catalyst, alkanes can form carbenium ions in different ways, such as by abstraction of hydride ions at a Lewis acid site[29, 99], by proton addition to the olefin intermediates, by hydride transfer with another carbenium or by protonation of paraffins on very strong Bronsted acid sites[83]. Once carbeniums are formed, they can undergo several reactions leading to isomerization and/or cracking. The carbenium ions formed on acid sites lead to skeletal isomerization by internal hydrogen and alkyl shifts to form stable tertiary cations. β-scission occurs and is considered to be an essential step leading to cracking reactions. As shown below, β-scission refers to the C-C bond cleavage in the β–position to the carbon atom carrying the positive charge of a carbenium ion. [100]

$$R_1\text{-}CH_2\text{-}CH^+\text{-}R_2 \xrightarrow{\beta\text{-scission}} R_1^+ + CH_2{=}CH\text{-}R_2$$

However, β-scission involves the production of primary carbenium ions which have very high energies of activation and is not likely to proceed at any significant rate under relatively mild conditions. And it does not provide satisfactory explanations for some experimental results, such as the low formation of C1 and C2 hydrocarbons, the strong branching in the cracked paraffin fractions, and the strong increase of cracking reactivity with carbon numbers above seven[101]. Sie [101-103] proposed a new mechanism which assumes a protonated cyclopropane (PCP) as the reaction intermediate in describing the hydroisomerization and hydrocracking process over acid catalysts, as shown in Figure 4. Hydroisomerization and hydrocracking via PCP avoid the generation of any primary carbenium ion.

This new mechanism not only cast a new light on the relation between hydroisomerization and hydrocracking, but it is also capable of providing a better explanation for many experimental facts which have not previously been explained in a satisfactory way.

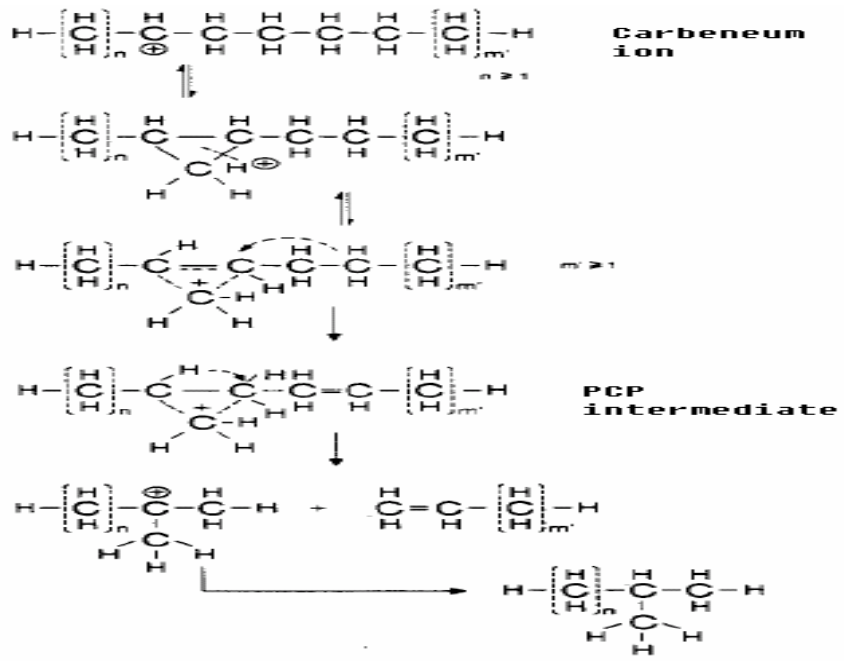



**Figure 4. Mechanism of Acid-catalyzed Hydrocracking of Normal Alkanes According to Sie**

It has been also found that the isomerization and cracking of heptane and heavier paraffins differ from that of the lighter paraffins. [24, 52] Not all of the experience obtained with experiments using light paraffins is applicable to heavy paraffins. Wang et al. found that the hydrocracking ability of a Pt-promoted sulfated zirconia catalyst was severely reduced when an olefin of the same carbon number as the paraffin feed, such as *n*-$C_7$ and *n*-$C_{16,}$ was added [58, 59]. This suggests that hydroisomerization and hydrocracking of long-chain normal paraffins over Pt-promoted modified zirconia catalysts may not involve a bifunctional mechanism in which the metal plays a hydrogenation/dehydrogenation role resulting in olefinic precursors to carbenium ions. In converting long-chain paraffins, the anion-modified zirconia may follow a mechanism other that the bifunctional one.

## 2.4 ROLES OF PLATINUM AND HYDROGEN

Anion-modified zirconia catalysts, such as sulfated zirconia and tungstated zirconia have catalytic activities for the isomerization and cracking of paraffin under mild conditions. These catalysts usually need a noble metal promoter, such as platinum[37, 38, 104], to increase their stability and reactivity. The presence of both platinum and hydrogen is important to keep the catalyst stable and active [50, 105, 106]. It is generally believed that a metal promoter activates hydrogen and keeps the active sites from deactivation by coke formation.[43-48, 107] Without platinum on the catalyst, hydrogen is scarcely adsorbed and activated. [107]

Platinum-promoted sulfated zirconia is often regarded as a bifunctional catalyst by many researchers. [8, 25, 50, 51] They proposed that platinum provides a metallic function and sulfated zirconia provides an acidic function. These two functions were related to the reaction processes of paraffin isomerization as in Figure 5. Dehydrogenation of the paraffin occurs on the metal surface; isomerization and cracking of the protonated paraffin, i.e. the carbenium ions, occur on the acid sites, and hydrogenation of the generated olefins takes place on the metal surface [108]. Both hydrogen and metal components play important roles in the process. However, in studying the conversion of hydrocarbons, bifunctional mechanism is only one of the many mechanisms that have been proposed. Recent research has resulted in modifications of a bifunctional mechanism.

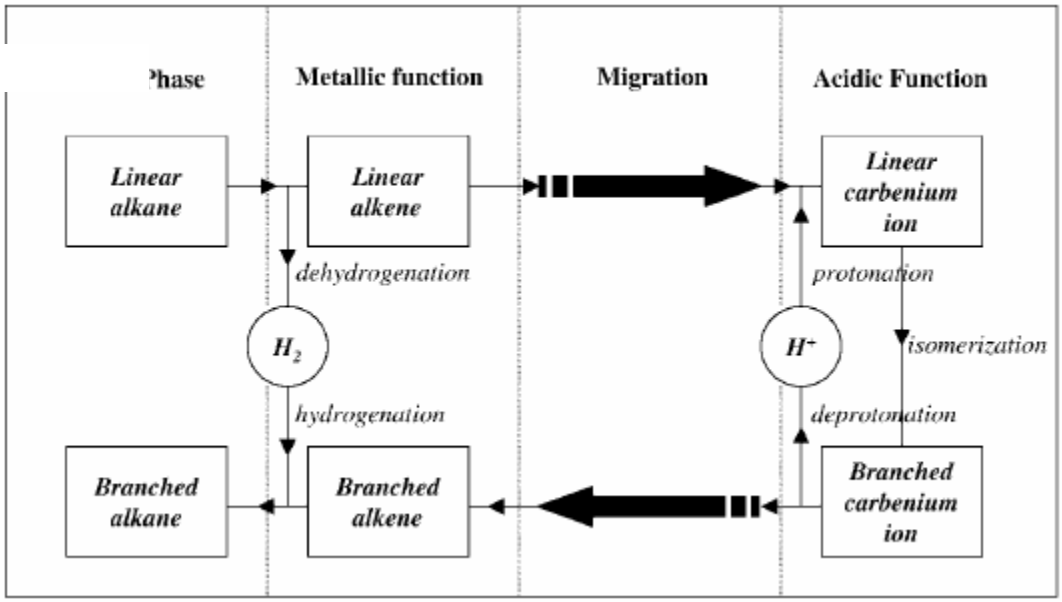



**Figure 5. Proposed Roles of Metal and Hydrogen in Alkane Isomerization**

Demirci et al. [50, 109] and Sachtler et al. [110-112] proposed that a structure termed a "metal-proton adduct" is the active site. In their work with zeolite-supported transition metals, Sachtler and his co-workers obtained evidence that zeolite protons and metal clusters can interact to form a "metal-proton adduct". On such active sites, all reaction steps of n-butane and n--pentane isomerization can take place with one "single residence" of the molecule. The reaction intermediates do not have to move between the metal and acid sites. It was found that the reactions catalyzed by these adducts are more rapid than those catalyzed by physically separated metal and acidic sites.[110, 113]

Demirci et al. [50, 109] proposed the hydrogen-metal-proton adduct structure, noted as ($[H_2\text{-}(M)\ (H^+)_x]^{x+}$) for platinum on sulfated zirconia in studies of the isomerization of n-heptane, n-octane and n-nonane. The effect of hydrogen was taken into account in the model shown in Figure 6.

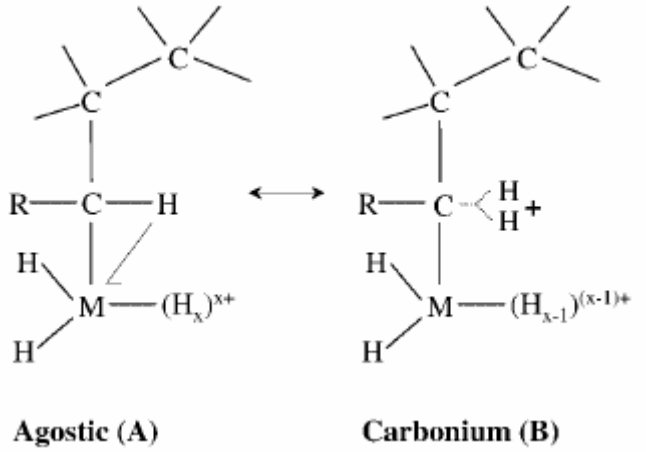



**Figure 6. Conversion of Paraffins over Platinum-proton-adduct Structure ($[H\text{-}(M)\ (H^{+})_{x}]^{x+}$) [50]**

The proposed adducts are active sites that combine the metallic and acidic sites. The word "agostic" is used to refer to these adduct active sites, where a hydrogen atom is covalently bonded simultaneously to both a carbon atom and a transition metal atom, as in Figure 6A. After the paraffin is associative adsorbed, an agostic site activates the paraffin to form a carbonium ion, as shown in Figure 6B. An adduct site demonstrates a metallic or an acidic function according to the hydrogen pressure. With hydrogen pressure higher than 760 Torr, the metallic part of the adduct shifts to the acidic one. At low hydrogen pressure, the paraffin is activated by the metallic function of the adductive site; at high hydrogen pressure, by its acidic site.

The influences of platinum and hydrogen on the acidity of anion-modified zirconia catalysts have been observed and various theories proposed. Shishido et al. reported the promotion effect of molecular hydrogen on Pt-promoted sulfated zirconia catalyst using IR spectroscopy of adsorbed pyridine and TPD of hydrogen and deuterium. [67, 107] They proposed

that molecular hydrogen dissociates on the platinum component to form hydrogen atoms, which spillover to the support and are absorbed on Lewis acid sites. The hydrogen atom releases an electron and becomes a proton. The protonic acid sites thus formed act as active sites for acid-catalyzed reactions. By evacuation of hydrogen in the gas phase, reverse processes take place to restore the original Lewis acid sites and eliminate the protonic acid sites. The concentration of protonic acid sites on the surface can be changed by the gas phase hydrogen pressure. Without platinum, the promotional effect of hydrogen is not appreciable.

The same Pt and hydrogen interactions may also occur with Pt-promoted tungstated zirconia systems. In isotopic exchange experiments between n-heptane and deuterium, Iglesia et al.[26, 114]claimed that Pt-promoted tungstated zirconia is much more effective that Pt-promoted sulfated zirconia in activating and storing hydrogen atoms. They also suggested that this difference results in a longer residence time for surface carbocations on Pt-promoted sulfated zirconia, resulting in more extensive cracking and reduced isomerization selectivity.[26]

Instead of the promotional effect of platinum and hydrogen on acidity of sulfated zirconia[67, 107], Santiesteban et al. found a deleterious effect of platinum on tungstated zirconia in the presence of hydrogen. The generation of spillover hydrogen at room temperature, the development of a strong Pt-tungstate interaction and tungsten reduction were observed using hydrogen chemisorption and TPD tests. The strong Pt-support interaction occurs via partial reduction of the $WO_3$ species by spillover hydrogen. In the isomerization of n-pentane, the presence of platinum decreased the acid activity of tungstated zirconia by facilitating tungsten reduction. Similar roles of platinum on tungstated zirconia catalysts in the hydroisomerization of n-pentane were confirmed by other researchers and characterization tests of CO chemisorption and transmission electron microscopy were applied.[114] It was proposed that hydrogen

dissociatively adsorbs on platinum and reduces the tungsten species by hydrogen spillover, forming $W^{5+}$ centers. This proposal is in agreement with the theories of Iglesia et al. [26].

## 2.5 HYBRID CATALYSTS

Spillover is a very important phenomenon in heterogeneous catalysis. A definition of spillover was proposed in 1989 during The Second International Symposium on Spillover.[115] It was pointed out that spillover involves the transport of an active species ( "S" in Figure 7) adsorbed or formed on a first phase ( "A" in Figure 7) onto another phase ("B" in Figure 7) that does not adsorb or form the species under the same conditions. A schematic representation of spillover of a gaseous diatomic molecule from an adsorbing surface onto a non-adsorbing surface is shown in the next figure.[116] A reasonable energy level diagram for the processes is shown in Figure 7. The adsorbed species can move across the surface to the interface with the second surface.

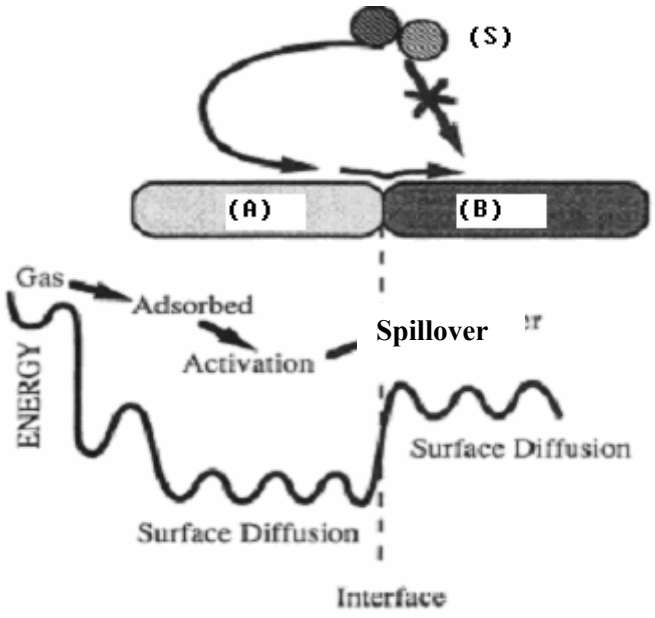



**Figure 7. Schematic Representation of Spillover Process**

Many of the spillover processes were clearly demonstrated in the use of mixtures of catalysts, referred to as hybrid catalysts. In many cases hybrid catalysts yielded better catalytic results than either of the individual components used separately. It has been reported that spillover of hydrogen and other species plays critical roles in the hydroisomerization and hydrocracking of normal paraffins. [6, 38, 39, 64, 65, 116-118]

It is known that isomerization or hydrocracking of paraffins occurs quickly on solid acid catalysts promoted by a noble metal under a hydrogen atmosphere. In a study of isomerization of n-$C_5H_{12}$, Fujimoto et al. [65] reported that a physical mixture of Pt/$SiO_2$ and H-ZSM-5 showed high activity and selectivity equal to those of Pt/ZSM-5 while Pt/$SiO_2$ and H-ZSM-5 alone had a poor catalytic performance for this reaction. In the absence of hydrogen, the conversion of n-$C_5H_{12}$ was dramatically reduced. These results and the fact that an intimate mixing of the hybrid components is needed to generate isomerization activity suggested that spillover hydrogen (proton and hydride) plays an important role in paraffin activation and in the

stabilization of intermediates. In a following paper [39], a spillover model of the process was proposed as shown in Figure 8. The spillover hydrogen presumably exists on a zeolite surface as proton and hydride. The protons act as the acid and abstract hydride ions from n-pentane or attack the carbon atom directly to promote isomerization or cracking. The n-$C_5H_{11}^+$ is isomerized to iso-$C_5H_{11}^+$ and then iso-$C_5H_{11}^+$ is stabilized by hydride addition. With regard to the generation of an active site by spillover species, Ebitani et al.[49] presented evidence of spillover hydrogen migrating from metal to sulfated zirconia to initiate a protonic acid site.

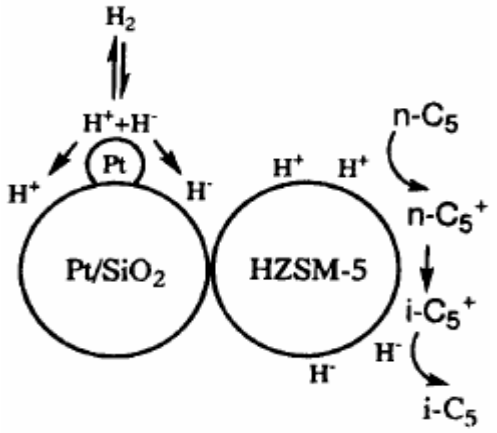



**Figure 8. Proposed Spillover Model for the Hydroisomerization of n-Pentane over a Hybrid Catalyst**

Vasina et al. [64] observed a similar result using hybrid catalysts consisting of $Pt/Al_2O_3$ and FAU zeolites. Under the same reaction conditions, the reactivities and selectivities of the hybrid catalyst for the isomerization of n-$C_6H_{14}$, n-$C_8H_{18}$ and n-$C_{14}H_{30}$ are close to that of the Pt/FAU catalyst. In the hybrid catalyst, the metal and acidic functions are separated spatially. In the Pt/FAU catalyst, the metal and acid centers are in close vicinity. The similarity in the performances of the two types of catalysts was explained by the high rate of spillover of

hydrogen and other reactive species such as reaction intermediates. In the study of the conversion of paraffins from C7 to C12 using a 0.3% Pt-promoted mordenite catalyst (Pt/H-Mor) at 250°C and 1.5 MPa, Grau et al.[6]found that coke deposition increased with the increase of the chain length of the reactants. When platinum is deposited on $Al_2O_3$ particles which are then physically mixed with H-MOR particles, the beneficial effect of platinum of the composite catalyst is greater than that when platinum is deposited on H-MOR. In a comparison of H-MOR+ $Pt/Al_2O_3$ with Pt/H-MOR catalysts having the same average platinum concentration, the activity and selectivity to iso-paraffins of composite catalysts are always higher and coke deposition lower. They proposed that the unsaturated coke precursors produced on the platinum in Pt/HMOR are adsorbed on the acid sites of the support producing coke and deactivating the surface. But the coke precursors produced on the metal function of $Pt/Al_2O_3$ can be partially adsorbed on neighboring inactive sites of $Al_2O_3$. These coke precursors, because of their large size, cannot diffuse easily to the pores of H-MOR, but they can diffuse out of the catalyst.

The spillover effect is not limited to the surface adjacent to the interface but also has a long-range effect. As the easiest spillover process, hydrogen spillover has been reported over distances as large as 1 cm in a $Pt/Al_2O_3$ (0.5 wt % Pt) and H-mordenite hybrid catalyst. [115, 116] This measurement demonstrates how readily spillover can take place. Although most studies of spillover have focused on hydrogen and oxygen species, multi-atom species have also been detected on supports as a result of spillover. Although only the spillover of hydrogen and oxygen have been shown to have influence on the oxide (support) surfaces, there is no reason that spillover of other species will not also react with accepting surfaces to modify the catalytic activity. The surfaces that have been induced to possess unique sorption and catalytic properties include silica, alumina, other transition metal oxides, and zeolites. The combined system can

exhibit catalytic capabilities that are greater than the sum of those of the individual components. [116] To be specific, it is very likely that favorable spillover of hydrogen and hydrocarbon species are involved in hybrid catalysts consisting of materials such as $Al_2O_3$, $SiO_2$ and zeolite.

There have been reports of the use of sulfated zirconia as a component of hybrid catalysts in the investigation of hydroisomerization and hydrocracking of paraffins. [62, 64, 118] Vasina and co-workers prepared hybrid catalysts by mechanically mixing $Pt/Al_2O_3$ (1 %Pt on γ-alumina) and sulfated zirconia (5% $SO_4$). The ratio of the components in the mixture was 1:1. Catalytic testing was performed on the isomerization of n-hexane in a flow unit at 220-280°C, LHSV =1 $h^{-1}$, pressure of 0.1 MPa and a hydrogen : n-hexane ratio = 6:1 mole/mole. The catalyst loading was fixed as 2 ml. While both $Pt/Al_2O_3$ and sulfated zirconia exhibited low activity, less than 5%, under the given conditions, the combination of the two components in the hybrid system led to an increase in activity; a conversion of 76.7 % was obtained at 280°C. In a study comparing normal butane isomerization with Pt-promoted sulfated zirconia and a hybrid catalyst, physically combining Pt/SiO2 and sulfated zirconia, Tomishige et al. [41] found that the two catalysts demonstrated similar reactivities and responses to hydrogen. It is claimed that the effective spillover in the hybrid system allowed separation of the metal and acid sites.

Hybrid catalysts containing Y zeolites as the main components and sulfated zirconia as a co-catalyst have been studied by Xiao and Le Van Mao[62] for hydrocracking of n-octane. They used 10 wt% of bentonite clay as a binder to a mixture of 50 wt% Pt/Y-zeolite (0.5 %Pt) and 40 wt% sulfated zirconia. After adding water, the hybrid catalyst was obtained by extrusion followed by drying at 120°C and calcination at 400°C for 12 hours. After combination with Y zeolite, sulfated zirconia significantly improved catalytic performance. The explanation suggested was that the sulfated zirconia transfers some of the incomplete hydrocracking

intermediate, such as isomers of n-octane to the zeolite surface. These intermediates then undergo further isomerization and cracking on the zeolites acid sites. Sulfated zirconias have more acidic and open structures than microporous Y-zeolites. The higher n-octane adsorption rate and fewer diffusion problems make sulfated zirconia a good co-catalyst. It was proposed that several properties of the co-catalyst can affect the performance of the hybrid catalyst. The importance of these properties follows the order of surface acidity, surface area and openness of the pore system.

# 3.0 RESEARCH OBJECTIVES

The main objective of this research is to study the use of Pt-promoted anion-modified zirconia catalysts in the conversion of the long-chain paraffins, such as those in Fischer-Tropsch (FT) waxes, into transportation fuel products. Although FT gasoline is also a desirable product, special emphasis has been put on a more challenging effort, which is to obtain middle distillates within the range of jet and diesel fuels. Long-chain paraffins, such as n-$C_{24}$ or n-$C_{36}$, were used as model compounds for testing the various catalysts in a microautoclave reacting system.

Some specific goals were as follows:

1. Evaluate and compare the performance of Pt-promoted tungstated zirconia and Pt-promoted sulfated zirconia catalysts.
2. Determine the effects of reaction conditions, such as temperature and hydrogen pressure, on the reactivities and selectivities of the two types of anion-modified zirconia catalysts.
3. Investigate the use of combination catalysts consisting tungstated zirconia and sulfated zirconia, for obtaining optimum hydroisomerization and hydrocracking functions for high yields of middle distillate products.
4. Examine and compare several different methods of synthesizing hybrid catalysts.

5. Explore the influence of catalyst (such as component type and ratio) and reaction condition (such as hydrogen pressure) on product distribution using hybrid catalysts.
6. Gain a better understanding of the catalysts, especially the hybrid catalyst systems, with characterization tests.

With this work, we intended to demonstrate a new method for improving catalyst performance in converting FT waxes by using hybrid systems. There are many factors that affect the performance of the catalysts. These factors include the composition and type of catalyst, the preparation method and reaction conditions. In this exploratory research, we study and compare a number of catalyst systems under established reaction conditions (such as 200°C) and lay the foundation for further investigations. It is found that hybrid zirconia-based catalysts are effective and flexible for converting FT waxes to desired products.

# 4.0 PREPARATION OF PLATINUM-PROMOTED ANION-MODIFIED ZIRCONIA AND HYBRID CATALYSTS

## 4.1 OBJECTIVES

(1) To synthesize Pt-promoted tungstated or sulfated zirconia catalysts using different zirconia sources, i.e. in-house samples prepared in our laboratory or commercial sample obtained from a company (MEI).

(2) To prepare anion-modified zirconia catalysts promoted with various amounts of Pt.

(3) To use different methods to synthesize hybrid catalysts consisting of Pt-promoted tungstated zirconia(PtWZr) and sulfated zirconia components with various ratios.

(4) To synthesize hybrid catalysts consisting of PtWZr and zeolite components, such as mordenite, Y zeolite, Beta zeolite and amorphous silica-alumina, with various ratios.

Catalytic tests were carried out to evaluate and compare the prepared catalysts. For the convenience of experiment operation and product analysis, n-$C_{24}$ was used as the reactant in this part of research.

## 4.2 BACKGROUND

The activity of zirconia-based solid acid catalysts could be affected by many factors, such as the type of metal, the loading method of the metal precursors and the method of making and modifying the zirconia component. After comparing various preparation methods, the preparation method which gave the most active catalysts was chosen and further study was carried out using catalysts prepared with that particular procedure. Based on the results of previous work in our laboratory [55, 58, 93, 119, 120] and reports of other researchers, Pt was selected as the best metal promoters and was used with 0.5wt% concentration throughout this work. For tungstated zirconia catalysts, the $WO_3$ concentration was fixed at 12.5 wt% W when comparing the catalysts. For sulfated zirconia, the concentration of sulfate group was about 6 wt% in term of $SO_3$.

It should be noted that the catalytic properties of the solid acid catalysts may strongly depend on the preparation method. We prepared tungstated zirconia and sulfated zirconia catalysts in our laboratory and compared them with catalyst samples from Magnesium Elektron, Inc. (MEI) in the conversion of n-$C_{24}$.

## 4.3 EXPERIMENTAL

### 4.3.1 Chemicals and Materials

The starting chemical materials used for the synthesis of Pt-promoted anion-modified zirconias and hybrid catalysts are listed in the Table 1.

**Table 1. Starting Chemicals for Synthesis of Catalysts**

| Description | Chemical | Purity (%) | Source |
|---|---|---|---|
| **Starting Salt** | Zirconium tetrachloride | 99.9 | Strem Chemicals |
| | Zirconium sulfate | 99 | Pfaltz & Bauer |
| **Precipitating agent** | Aqueous ammonium hydroxide | 28 | Fisher Scientific |
| **Anionic Groups** | Ammonium metatungstate | 99.9 | Strem Chemicals |
| | Sulfuric acid | 97 | J.T. Baker |
| **Pt Precursor** | Chloroplatinic acid hexahydrate | 99 | Pressure Chemical |
| | TetraamminePt(II) chloride monohydrate | 99.9 | Strem Chemicals |

The commercial modified-zirconia samples were provided by MEI as dry, free-flowing powders. Samples of approximately the same composition were also prepared in our laboratories. Some of the properties of these samples are listed in Table 2. After calcination, 0.5 wt % Pt was loaded on the tungstated zirconia and sulfated zirconia samples when needed.

**Table 2 Properties of Anion-modified Zirconia Samples**

| **Properties** | **MEI Sample** | | **In-house Sample** | |
|---|---|---|---|---|
| | **Tungstated** | **Sulfated** | **Tungstated** | **Sulfated** |
| **Anion Group, on ZrO2** | 12.5 wt % W | 6 wt% $SO_3$ | 12.5 wt % W | 6 wt% $SO_3$ |
| **Surface Area, $m^2/g$, 650°C/2hrs** | 100 | 175 | 105 | 110 |
| **Pore volume, $cm^3/g$, 550°C/2hrs** | 0.2 | 0.2 | 0.2 | 0.2 |

We obtained three zeolites from Zeolyst International and two amorphous silica-alumina samples from Sasol. The relevant properties of these materials are listed in the following tables. To compare the effects of zeolite type on catalytic performance, we ordered zeolite samples with the similar Si/Al ratios.

**Table 3. Properties of Zeolite Samples from Zeolyst International**

| Zeolite Type | Mordenite (MOR) | Beta (BEA) | Y (FAU) |
|---|---|---|---|
| **Product Code** | CBV21A | CBV814E | CBV720 |
| **Abbreviation** | Mor21A | B814 | Y720 |
| **$SiO_2/Al_2O_3$ mole ratio** | 20 | 25 | 25 |
| **Surface Area, $m^2/g$** | 600 | 680 | 750 |

**Table 4. Properties of Amorphous Silica-alumina from Sasol**

| Product Name | Siral40 | Siral 20 |
|---|---|---|
| **Surface Area, $m^2/g$** | 500 | 420 |
| **$SiO_2/Al_2O_3$ ratio** | 40/60 | 20/80 |
| **Particle Size, d50, μm** | 38 | 50 |
| **Pore volume, $cm^3/g$,** | 0.9 | 0.8 |

### 4.3.2 Synthesis of Anion-modified Zirconia Catalysts

Two types of tungstate-modified and sulfate-modified zirconia were prepared. One was prepared in our laboratory; the other was provided by MEI. Same incipient wetness impregnation procedure was used to load Pt onto these modified-zirconia samples.

**4.3.2.1 Synthesis of Tungstated Zirconia Catalysts** The tungstated zirconia prepared in our laboratories was synthesized with zirconium hydroxide by adding ammonium hydroxide to zirconium chloride following these major steps:

(1) Dissolution: 125 g of zirconium chloride was added to 1000 ml of double-distilled water while the solution was being stirred for one hour at room temperature to form a solution about 0.5M.

(2) Hydrolysis: aqueous ammonia was added to the solution at the rate of 15 - 20 drops per minute with continuous stirring. When the pH value of the solution reached 10, the addition of ammonia was stopped and the solution was stirred for another 5 minutes and allowed to age overnight.

(3) Filtration and Washing: the supernatant solution was decanted and the precipitate filtered under vacuum using Whatman No. 1 filter paper. The filter cake obtained was dissolved in 1000 ml of double-distilled water and the solution filtered and washed to remove chloride ions and excess ammonium hydroxide. The operation was repeated to ensure that no chloride ions could be detected by 0.1 M AgNO3 solution.

(4) Drying: the washed filter cake of zirconium hydroxide was dried in an oven at 110°C overnight to remove water;

(5) Grinding: the dried precipitated zirconium hydroxide was ground using an agate pestle and mortar to a fine powder and the particles passing through a 100 mesh sieve were collected.

After the zirconium hydroxide powder was prepared, it was modified by impregnation of ammonium metatungstate solution following by drying at 110°C overnight and calcination at 700°C for 3 hours. The tungstated zirconia material was then ground and sieved again. This

tungstated zirconia contains 12.5 wt% W, which is the same as the tungstated zirconia prepared by calcination of MEI tungstate-doped zirconium hydroxide.

To load the Pt, the tungstated zirconia samples were impregnated with the solution of a Pt salt of the appropriate concentration. Then the mixture was dried at 110°C overnight and calcined at 550°C for 3 hours.

Figure 9 shows the preparation procedures described above.

4.3.2.2 **Synthesis of Sulfated Zirconia Catalysts** The procedures for preparing sulfated zirconia were slightly different from those used in preparing tungstated zirconia. Instead of zirconium chloride, zirconium sulfate salt was used in the solution to be hydrolyzed by aqueous ammonia. Using the starting salt with the sulfated group avoids the need to remove chloride ions in the solution and aids in the incorporation of the sulfated group with zirconia. After zirconium hydroxide powder was obtained, it was slurred for 1 hour in the 1N sulfuric acid solution. For each gram of zirconium hydroxide, 10 ml sulfuric acid solution was used. The slurry was filtered to remove excess water. The filter cake was then dried at 110°C overnight and ground to powder finer than 100-mesh. The sulfated zirconium hydroxide prepared in this way or that provided by MEI was then calcined at 600°C. The incipient wetness impregnation with the solution of a Pt salt of the appropriate concentration was used to load the Pt, followed by drying at 110°C overnight and calcination at 550°C for 3 hours. These preparation procedures are shown in Figure 10.

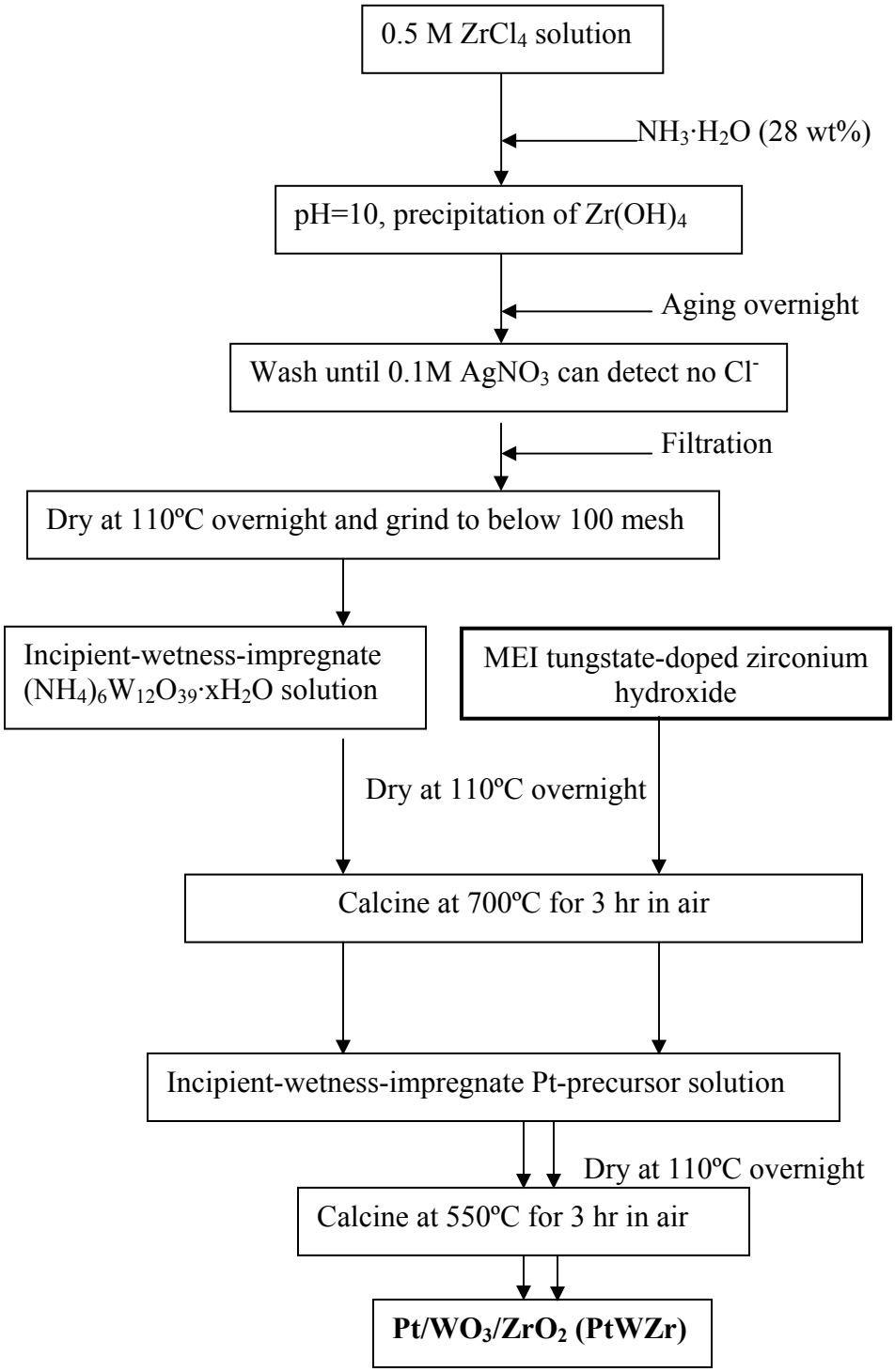



**Figure 9. Preparation Procedures for Preparing Tungstated Zirconia Catalysts**

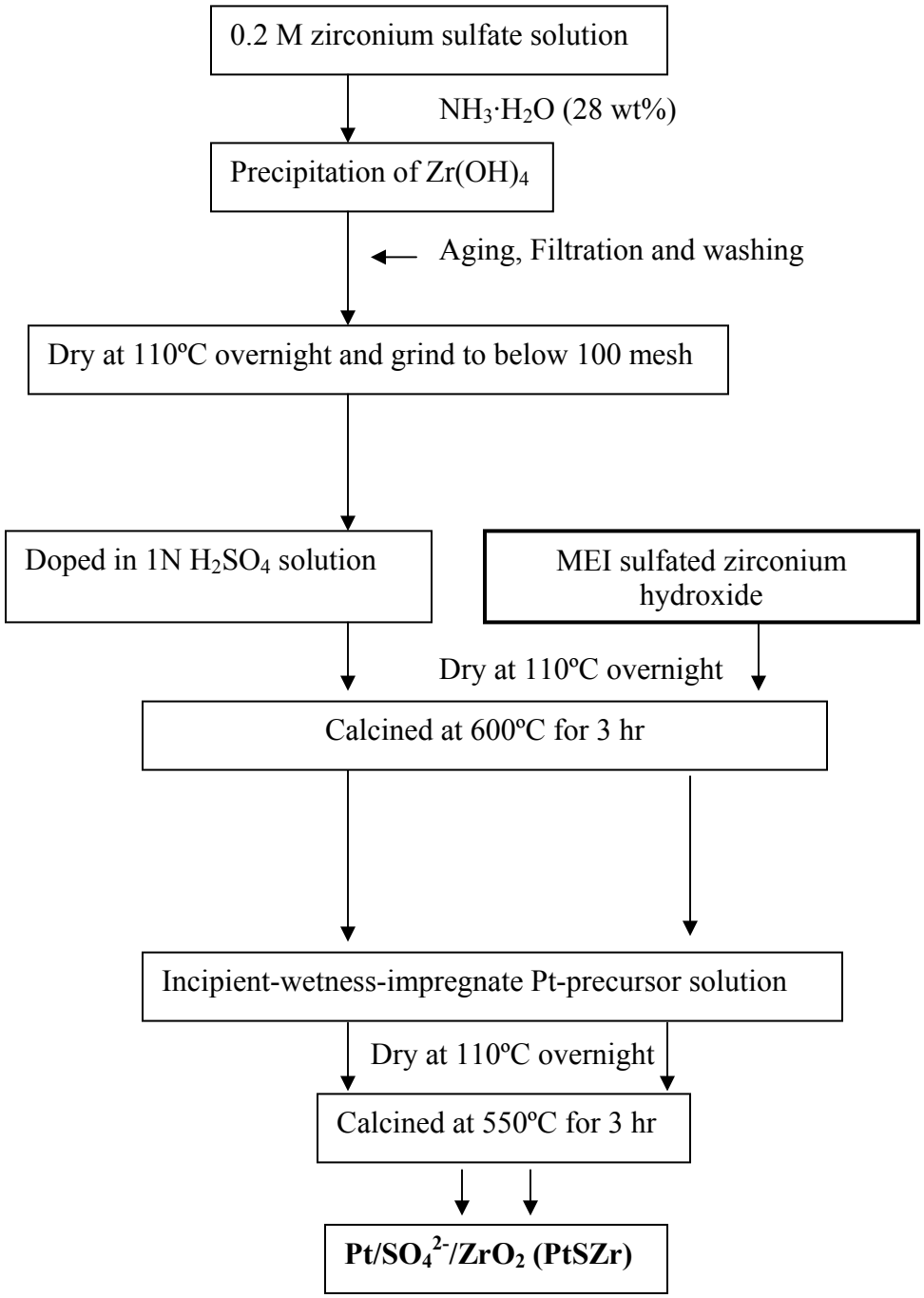



**Figure 10. Preparation Procedures for Preparing Sulfated Zirconia Catalysts**

### 4.3.3 Syntheses of Hybrid Catalysts

The term "hybrid catalyst" is used to designate a combination catalyst of a tungstated zirconium component and another component, such as a sulfated zirconia or zeolite catalyst.

#### 4.3.3.1 Hybrid Catalysts Consisting of Tungstated Zirconia and Sulfated Zirconia

Zirconia catalysts were prepared and ground using an agate pestle and mortar to be finer than 100 mesh before calcination at 550°C for 1 hour to remove any moisture. When necessary, Pt was loaded to the component following the same procedures described above.

Three types of combination methods were studied in preparing the hybrid catalysts:

a) "*Direct-addition*": Tungstated zirconia and the sulfated zirconia were activated by calcination separately and mixed directly inside the reactor without any extra mixing procedures before reaction;

b) "*Wet-mixing*": Tungstated zirconia and the sulfated zirconia component were slurried and shaken in an ultrasonic bath followed by drying overnight and calcination;

c) "*Dry-mixing*": Tungstated zirconia and the sulfated zirconia component were mixed and ground thoroughly using an agate pestle and mortar and then calcined.

All the calcinations were carried out at 550°C for 3 hours.

4.3.3.2 **Hybrid Catalysts Consisting of Tungstated Zirconia and Zeolite** This type of hybrid catalyst was prepared following the same methods described above.

## 4.4 COMMENTS

There are many factors in catalyst preparation that can affect the catalytic properties of the final catalysts. The factors include but are not limited to: precursors of the metal promoters, loading method, preparation method, the sources of zirconium hydroxide, the type of the starting salt, calcination conditions and storage and pre-treatment conditions.

For zirconia catalysts made in our laboratory and those from MEI samples, comparable performance was observed. See Figure 9, Figure 10 and Table 2 for the preparation steps and catalyst properties. The comparison of in-house and MEI catalysts was made with n-$C_{24}$ as the reactant, data are listed in Table 5. MEI samples were produced on a large scale and were therefore used in further experiments to avoid variation in catalysts from different batches.

The anion-modified zirconia catalysts we used in the rest of the research were all prepared from MEI samples.

**Table 5. Comparison of Properties of Catalysts Prepared In-house and from MEI**

| Catalyst | Source | Conversion (wt%) | Selectivity (wt%) | | |
|---|---|---|---|---|---|
| | | | $C_5$-$C_9$ | $C_{10}$-$C_{20}$ | iso-$C_{24}$ |
| PtSZr | In-house | 62 | 85 | 9 | 6 |
| | MEI | 61 | 82 | 10 | 8 |
| PtWZr | In-house | 46 | 3 | 7 | 90 |
| | MEI | 48 | 2 | 9 | 89 |

**PtSZr/n-$C_{24}$ = 1:12 wt, 15 min; PtWZr/n-$C_{24}$ = 1:4 wt, 25 min;**
**$P_{H2}$=300 psi, 200°C**

# 5.0 CATALYST CHARACTERIZATION

## 5.1 OBJECTIVES

The performance of a catalyst system depends on its physical and chemical properties, so that it is critical to investigate the relationship between the catalytic and material properties of the catalyst. This involves identification of various properties such as surface area, pore structure, metal dispersion, crystal structure, microscopy imaging and element distribution. The correlation of this information with catalytic behavior helps in understanding of the nature of the catalyst system and furnishes clues as to the mechanism of the reactions under study. We could also possibly identify important factors which could enable us to tailor the catalytic properties for a given catalyst system.

In this chapter, characterization results of typical catalysts studied in this work are presented. The techniques include BET surface area tests, CO chemisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Temperature-programmed desorption (TPD) analysis using ammonia as the adsorbate was carried out to measure the acidity of the catalysts.

Catalytic tests were carried out to evaluate and compare various catalyst samples. For the convenience of experiment operation and product analysis, n-$C_{24}$ was used as the reactant in this part of research.

## 5.2 BACKGROUND

As discussed earlier, there is no doubt that Pt-promoted anion-modified zirconia catalysts possess outstanding and unique catalytic properties for hydroisomerization and hydrocracking of normal paraffins. However, questions about the nature of the catalysts and reaction mechanisms are still under debate. It is possible that acidity is needed to form carbenium ions although there is evidence that a redox reaction could also result in carbenium ion formation. For a hybrid catalyst system consisting of more than one type of particles, it is particularly important to learn the features, such as the particle shape, dispersion and contacting conditions of the hybrid components.

## 5.3 EXPERIMENTAL

### 5.3.1 Measurement of Physicochemical and Structural Properties

5.3.1.1 **BET Surface Area and Pore Size Distribution** We characterized the BET surface area and pore properties of the catalysts with an Accelerated Surface Area and

Porosimetry (ASAP) system, ASAP 2010, manufactured by the Micromeritics Instrument Corporation. A small amount of catalyst sample, about 0.2-0.3 g, was weighed and loaded into a sample tube with a bulb end. After putting a filler rod inside the tube, the opening of the sample tube was blocked with a seal frit. Then the sample was degassed under vacuum at 90°C for 1 hour and then at 350°C till the pressure was less than 10 μmHg. There is a cold trap with liquid nitrogen for elimination of moisture in the degas system. After cooling and backfilling with nitrogen, the sample tube assembly was weighed and the precise weight of the sample calculated by subtracting the weight of the empty tube assembly. Physisorption with nitrogen was carried out in an insulated liquid nitrogen bath, at about -196°C. The adsorption and desorption isotherms were then obtained automatically using the software of ASAP 2010 for Windows®, v. 4.01 Beta. The surface area and pore properties of a sample are presented in a report at the end of the analysis.

5.3.1.2 **Pt Conditions Measured by CO Chemisorption** The Pt dispersion was the percentage of active Pt atom (as detected by CO adsorption) in the total amount of Pt on the catalyst. To measure Pt dispersion of the catalysts, we used a Micromeritics® ASAP 2010 System manufactured by Micromeritics Instrument Corporation. This system controls measurement procedures automatically. The software used was ASAP Chemisorp 2010C 3.01. For each experiment, a catalyst sample was weighed and loaded in a U-shape quartz sample tube. To hold the sample powder in place, we used some quartz fiber to block both ends. The catalyst sample, usually 0.5 – 0.7 g, was reduced by hydrogen in the sample tube before chemisorption using carbon monoxide. The reduction temperature was set to 200°C, which is close to our

typical reaction temperature. The chemisorption of CO was carried out at 35°C. The surface area (m2/gsample) of Pt can also be measured with the same process.

5.3.1.3 **Crystallographic Phases Measured by Powder XRD** A Philips X'pert® X-ray diffractometer system was used to analyze crystallographic conditions of the bulk phase of catalyst samples. A ½° beam slit was applied to the CuKα radiation source ( λ= 1.5406 A) under 40 kV and 30 mA. With the automatic control of X'pert® Data Collector software, a line-focused continuous absolute-scan with Gonio-axis was carried out on each sample. The scan was from 5° to 75° in a 2θ-angle with a scan speed of 0.04° per second and the step size of 0.02°. The sample was prepared as a compact wafer within a mold and was then planted to a clip holder on the testing stage. After the data was collected, we used X'pert® Graphics & Identify software to analyze and process the XRD peaks.

5.3.1.4 **Surface Features Measured by SEM and EDX** Microscopy images of the catalyst surface were obtained using an XL 30/FEG system manufactured by Philips Electronics (Netherlands). The instrument is a Philips XL series scanning electron microscope equipped with a field emission electron gun (source), a secondary electron detector, a backscattered-electron detector and an EDAX® CDU™ LEAP™ detector. A small amount of catalyst powder was spread on double-side carbon tape stuck on a stub, which was then fixed to the sample holder. To avoid charge accumulation over the sample surface, which would cause noise in obtaining a quality image, a conductive coat was put on before the SEM test. A layer (about 5 nm) of palladium was placed on the surface of the sample using a HUMMER 10.2

sputtering system. After placing the prepared sample into the testing chamber which is protected with nitrogen gas, the vacuum was reduced to 10-9 bar. A 10-20 kV voltage was applied to generate the desired SEM images. Professor J. R. Blachere of the Material Science and Engineering Department provided assistance and constructive suggestions with our SEM tests. In addition to the SEM test, energy dispersive x-ray analysis (EDX) analysis was used with the same setup to identify the major element distribution of any spot over the sample. Using EDX, we can identify the composition of particles of interest on a SEM image.

### 5.3.2 Measurement of Acidic Properties by TPD

To characterize the acidic properties of catalytic samples, temperature programmed desorption (TPD) was used with ammonia as the absorbate molecule. The catalyst sample was loaded into a sample tube and pretreated in-situ at 500°C for 1 hour with a helium flow of 50 ml/min. The sample was then saturated with ammonia at 100°C for 10 min and then flushed with helium for 1 hour to remove the physically adsorbed ammonia molecules. The temperature was then raised to 700°C with a 10°C/min ramp with helium flow. The desorbed ammonia was detected using a thermal conductivity detector (TCD). The area of the desorption-peaks was related to the number of the active acid sites; the temperatures at which the peaks appeared were related to the strength of the acid sites. Mass spectroscopy was used to identify the desorbed species.

## 5.4 RESULTS AND DISCUSSION

### 5.4.1 Effects of Pt Loading on Properties of Catalysts

The role of Pt on solid acid catalysts has been recognized as a critical factor by several researchers[6, 29, 47, 49, 107, 121-123]. Although many theories have been proposed, the complicated functions of a Pt promoter are still unclear. We utilized CO-chemisorption and $NH_3$-TPD to study effects of Pt. SEM/EDX was also used in detecting the Pt component of the catalysts, but results were not definitive due to the low concentration (0.5 wt %) of Pt. In this work, Pt loading to a catalyst component was fixed at 0.5 wt% in comparing various catalyst systems

5.4.1.1 **Pt Concentration, Surface Area and Dispersion** Surface area and dispersion of Pt species over the catalyst surface are two important factors that may influence metal functions. The data in Figure 11 show that both Pt surface area and Pt dispersion over tungstated zirconia catalysts were affected by the concentration of Pt. But the trends were different. With Pt concentration from 0.25 wt% to 1.0 wt%, the Pt dispersion decreased from 72.5% to 3%; however, the Pt surface area (per gram of catalyst sample) reached a maximum (0.73 m2/g.sample) at about 0.5 wt% Pt concentration. As shown in Table 6, the reactivity of PtWZr catalysts with 0.25 wt% Pt is higher than that with 0.5 wt% Pt in n-$C_{24}$ conversion, which suggests that the activity of Pt is more related to Pt dispersion rather than to its surface area. The

PtWZr catalysts studied in this research have 12.5 wt% W. As shown in Figure 11, samples with 0.5 wt% Pt have a dispersion of 58.8%. In previous work(120) of Zhang, another PtWZr catalysts with a different tungstate concentration (6.7 wt% W) was studied. With the same 0.5 wt% Pt loading, that PtWZr sample had a Pt dispersion of 54.4%. The concentration of tungstate species does not affect Pt dispersion of PtWZr (0.5wt% Pt) significantly.

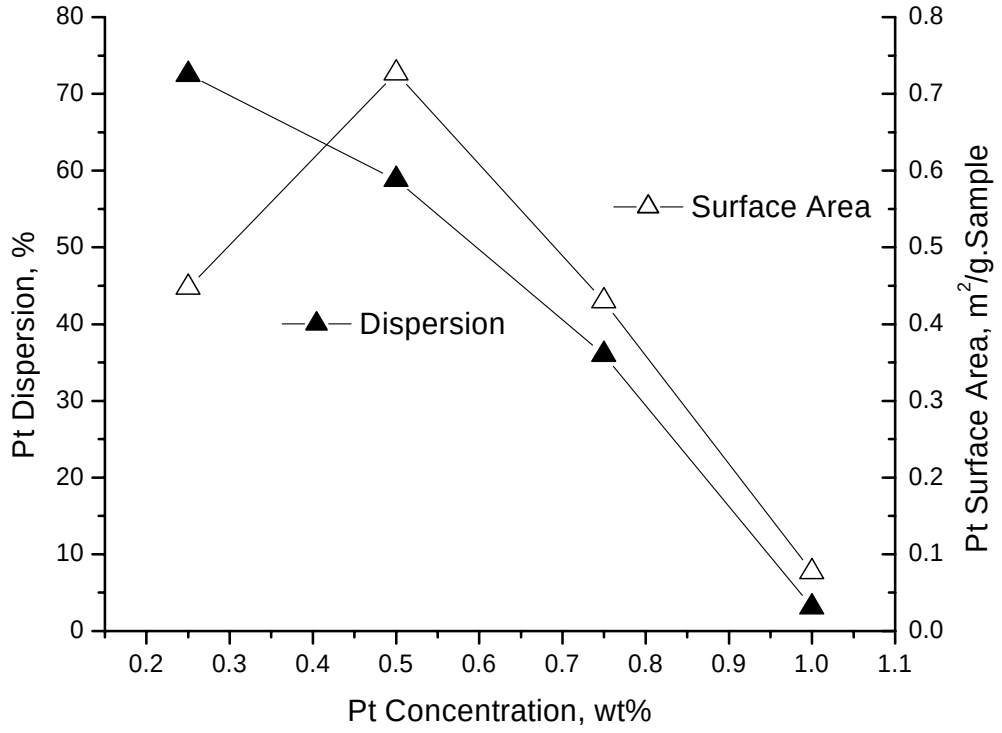



**Figure 11. Effect of Pt Concentration on Pt Distribution and Pt Surface Area over Tungstated Zirconia**

**Table 6. Comparison of PtWZr with 0.25 and 0.5 wt% Pt-loading**

| PtWZr | Pt dispersion, % | Pt Surface Area, $m^2$/g.Sample | n-$C_{24}$ conversion, wt% |
|---|---|---|---|
| **0.25 wt%Pt** | 72.5 | 0.45 | 50 |
| **0.5 wt%Pt** | 58.8 | 0.73 | 29 |

**0.25 g of each catalyst used; 1.0 g n-$C_{24}$ reactant; 200 °C, $P_{H2}$ = 500 psi, 20 min.**

It was also found that catalysts may have very different performance even with the same Pt concentration and similar Pt dispersions. For example, we compared two catalysts with the same overall chemical composition. (Table 7). For PtWZr (0.25 wt% Pt), Pt was loaded to WZr as normal; for a hybrid PtWZr/WZr(1:1) catalyst, only half of the WZr was loaded with Pt. PtWZr (0.5 wt% Pt) was mechanically mixed with an equal amount of WZr (no Pt). The overall concentrations of Pt (0.25 wt%), W (12.5 wt%) and Zr were the same for the two catalysts. The Pt dispersions and surface areas together with the n-$C_{24}$ conversions and selectivities of the two catalysts are shown in Table 7.

**Table 7. Comparison of PtWZr and PtWZr/WZr (1:1), both with 0.25 wt% Pt-loading**

| Catalyst with 0.25 wt%Pt | Pt dispersion, % | Pt Surface Area, $m^2$/g.Sample | n-$C_{24}$ conversion, wt% | Selec. to $C_{10}$-$C_{20}$ products, wt% |
|---|---|---|---|---|
| **(0.25 %Pt)PtWZr** | 72.5 | 0.45 | 50 | 7 |
| **(0.5%Pt)PtWZr/ WZr (1:1)** | 78 | 0.48 | 68 | 30 |

**0.25 g catalyst used; 1.0 g n-$C_{24}$ reactant; 200 °C, $P_{H2}$ = 500 psi, 20 min.**

With the same overall 0.25 wt% Pt-loading, the two catalysts in Table 7 have similar values for Pt dispersions and Pt surface areas. However, they show different performance in converting n-$C_{24}$ into middle range hydrocarbons. The hybrid PtWZr/WZr(1:1 wt) catalyst not only had a higher reactivity than PtWZr, but its selectivity to middle range products was also greater that that of the pure PtWZr catalyst. The configuration of the hybrid catalyst has special properties which facilitate increased activity and selectivity to $C_{10}$ to $C_{20}$ products. This result showed that the configuration of the hybrid catalyst can change catalytic performance with the same overall chemical composition and Pt conditions.

5.4.1.2 **Effect of Pt on Acidity** As stated earlier, tungstated zirconia is a weaker acid than is sulfated zirconia. The difference in acidity of these two materials is clearly shown in the TPD analysis with ammonia as the adsorbate. The larger area of the desorption-peaks of sulfated zirconia and the higher temperature at which the peaks appear in Figure 12 suggests that sulfated zirconia has a larger number of active acid sites and is a stronger acid than tungstated zirconia.

The acidities of these two materials are affected by Pt-loading in different ways. As shown in Figure 13, after being loaded with 0.5 wt% Pt, the tungstated zirconia has a TPD peak at a similar temperature range (100°C to 550°C), with a maximum at about 200°C. This result suggests that the acidic strength of tungstated zirconia is not significantly affected by Pt loading. The larger peak area of PtWZr shows that the total number of acid sites is slightly increased after Pt was loaded on to WZr.

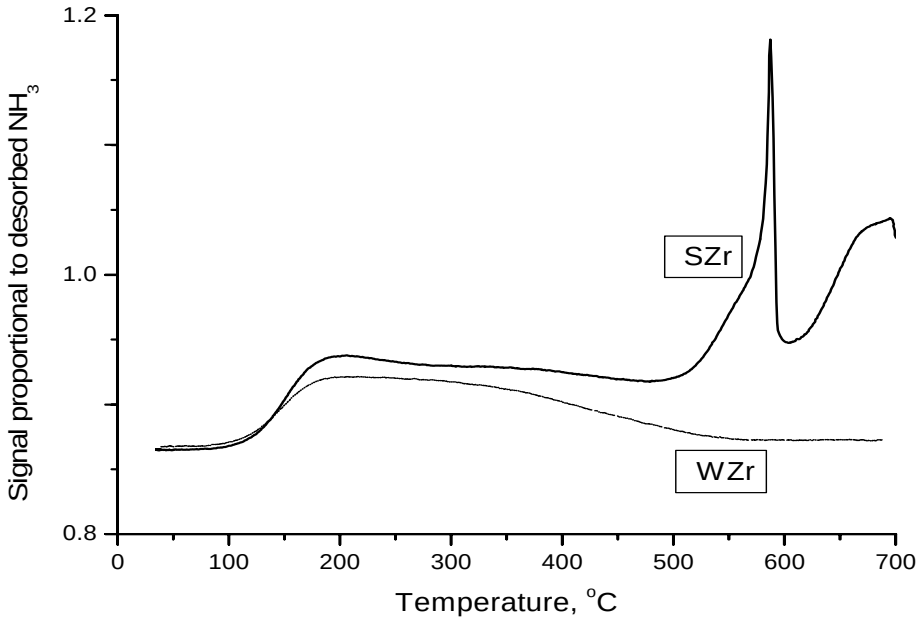



**Figure 12. Comparison of Acidities of Tungstated and Sulfated Zirconia**

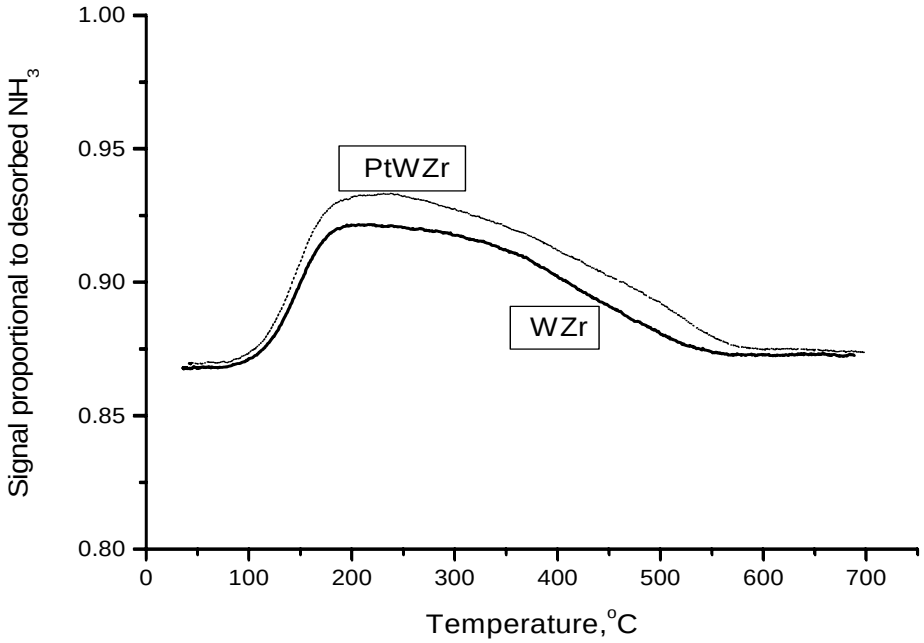



**Figure 13. Effect of 0.5 wt% Pt-loading on the Acidity of Tungstated Zirconia**

The sulfated zirconia results are different from those of tungstated zirconia. As shown in Figure 14, after being loaded with 0.5wt% Pt, the PtSZr showed the highest TPD peak at about 530°C, which is lower than 600°C as was the case for SZr. Moreover, the peak area of PtSZr is smaller than that of SZr. Both the number of acid sites and the acid strength of sulfated zirconia are decreased by Pt loading.

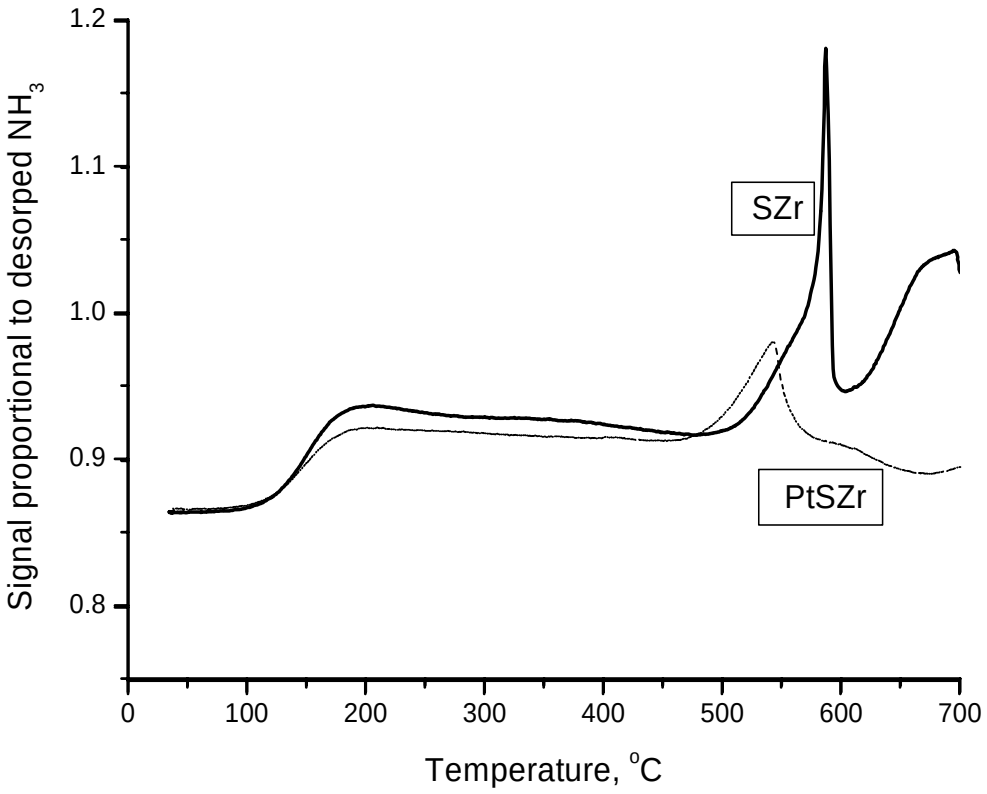



**Figure 14. Effect of 0.5 wt%Pt-loading on the Acidity of Sulfated Zirconia**

### 5.4.2 Effect of Hydrogen Reduction on Acidity

Before each reaction, the catalysts were reduced by hydrogen. The TPD with $NH_3$ was used to test the effect of hydrogen reduction on the acidities of PtWZr and PtSZr catalysts. The samples were reduced with 50 ml/min of $H_2$ (10%)/Ar, heated at 10°C/min to 200 or 400°C and then held for 60 minutes in hydrogen before the TPD tests.

The acidity of PtWZr before and after reduction with hydrogen are compared in Figure 15. After reduction, the area below the curve decreased. This shows that the number of the active acid sites on PtWZr decreased. The small difference between the curves of 200 and 400°C reduction shows the stability of PtWZr.

The effect of hydrogen reduction on PtSZr is different from that of PtWZr. As shown in Figure 16, PtSZr before reduction has a peak at about 530°C. After hydrogen reduction at 200°C, that peak moved to 500°C and became larger, suggesting an increased number of active acid sites. However, when PtSZr was reduced with hydrogen at 400°C, the peak around 500°C disappeared. High temperature reduction greatly affects the ability of PtSZr to adsorb the basic ammonia molecule.

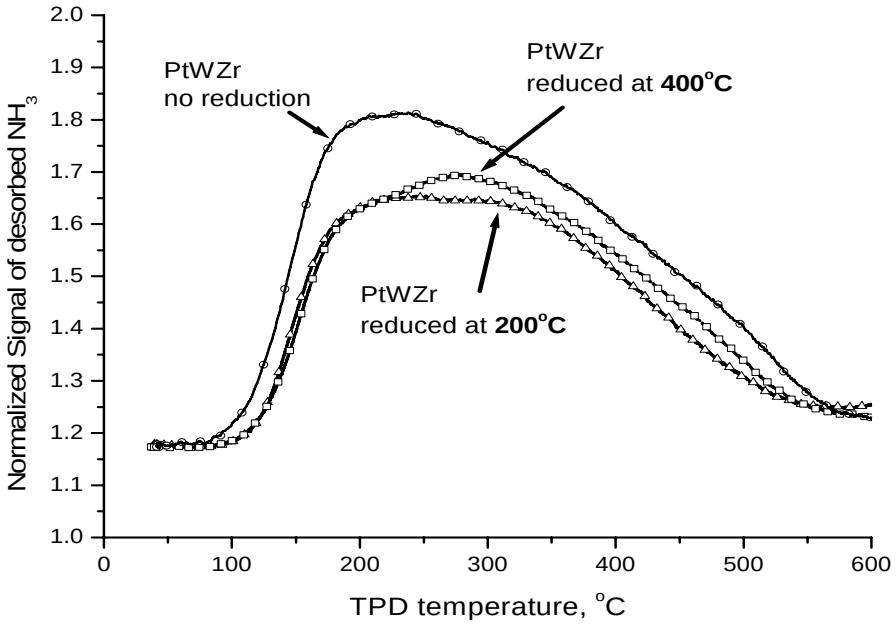



**Figure 15. Effect of Hydrogen Reduction on Acidity of PtWZr**

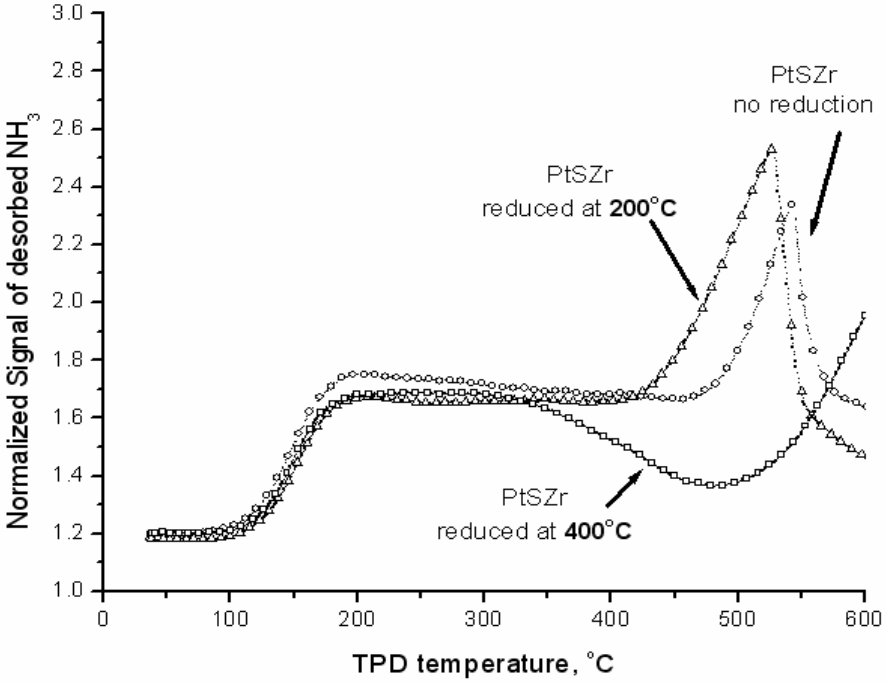



**Figure 16. Effect of Hydrogen Reduction on Acidity of PtSZr**

### 5.4.3 Hybrid Catalysts

We studied two types of hybrid catalysts; both have tungstated zirconia as one of the components. The second component is either a sulfated zirconia or a zeolite catalyst. Because the two types of particles in PtWZr/zeolite systems are much easier to be precisely identified, we carried out more SEM and EDX analysis on them than for PtWZr/SZr systems. Since the preparation of these two hybrid systems follows the same steps, they should share some similarities so that some of the characterization tests results of one system could be similar to the other system.

5.4.3.1 **Hybrid Catalysts of PtWZr and Zeolites** The zeolite materials we used to combine with PtWZr include mordenite, β zeolite, Y zeolite and amorphous silica-alumina samples, the properties of which are listed in Tables 3 and 4. Because these silica-alumina particles are very different in chemical compositions and physical shapes from those of tungstated zirconia, they are easily identified using SEM and EDX techniques in a hybrid catalyst. The SEM image of a PtWZr/Mordenite catalyst is shown in Figure 17. Particles of the two types of components are identified by EDX analysis, as shown in Figures 18 and 19.

In the SEM image of PtWZr/Mordenite sample shown in Figure 17, there are two types of catalyst particles, each with a different shape. The fine particles marked with “Mor” are either in clusters or are isolated. The other particles are much larger. EDX patterns were generated to examine and identify the element composition of particles on an SEM image.

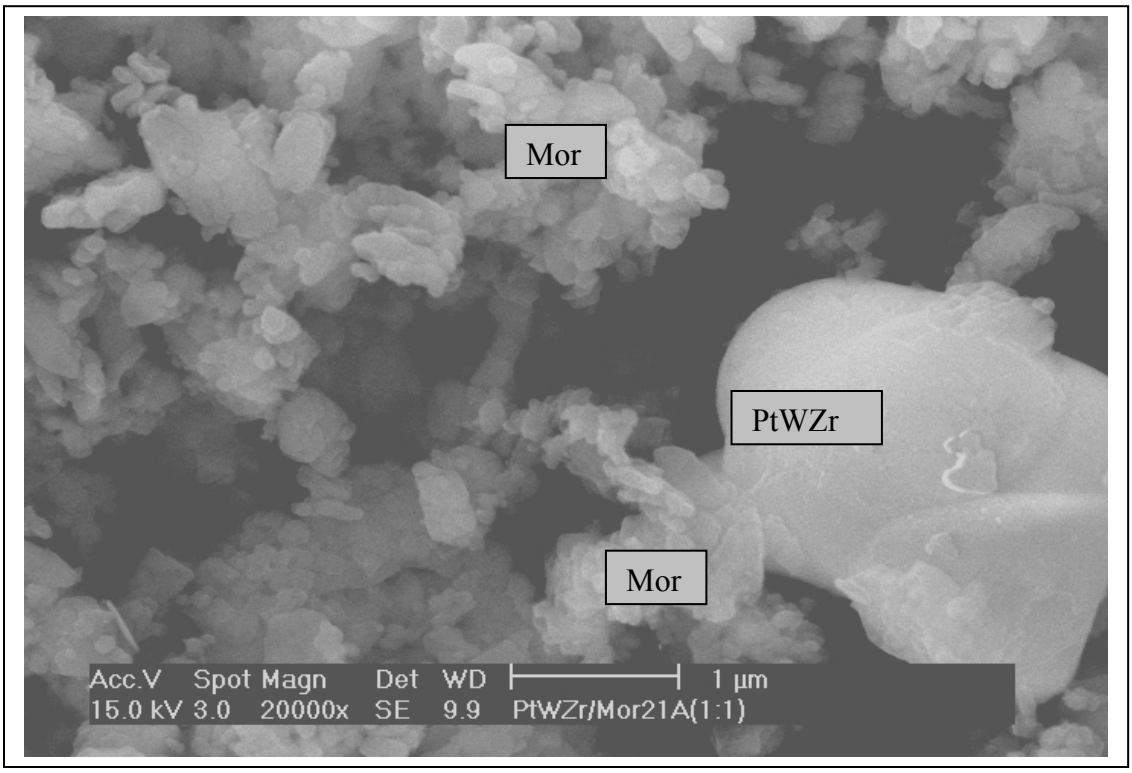



**Figure 17. SEM Image of a PtWZr/Mordenite(Mor) Catalyst**

The PtWZr particles have EDX patterns similar to those in Figure 18. There are three major characteristic peaks of oxygen, tungsten and zirconium. Pt cannot be identified because that the signals from small amounts of Pt (0.5 wt %) are too low and the location of the major Pt peak overlaps the large peak of zirconium.

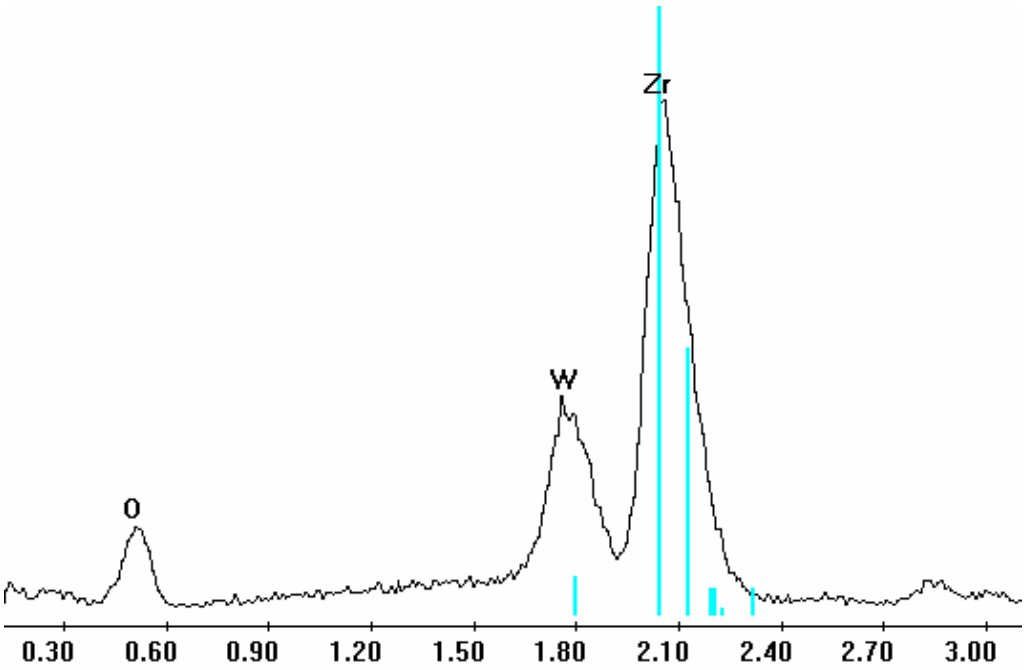



**Figure 18. EDX Spectrum of the Tungstated Zirconia (12.5 wt% W)**

The EDX peaks of a zeolite component are very different from those of PtWZr. As shown in Figure 19, the zeolite particles can be identified by their characteristic peaks of silicon and aluminum.

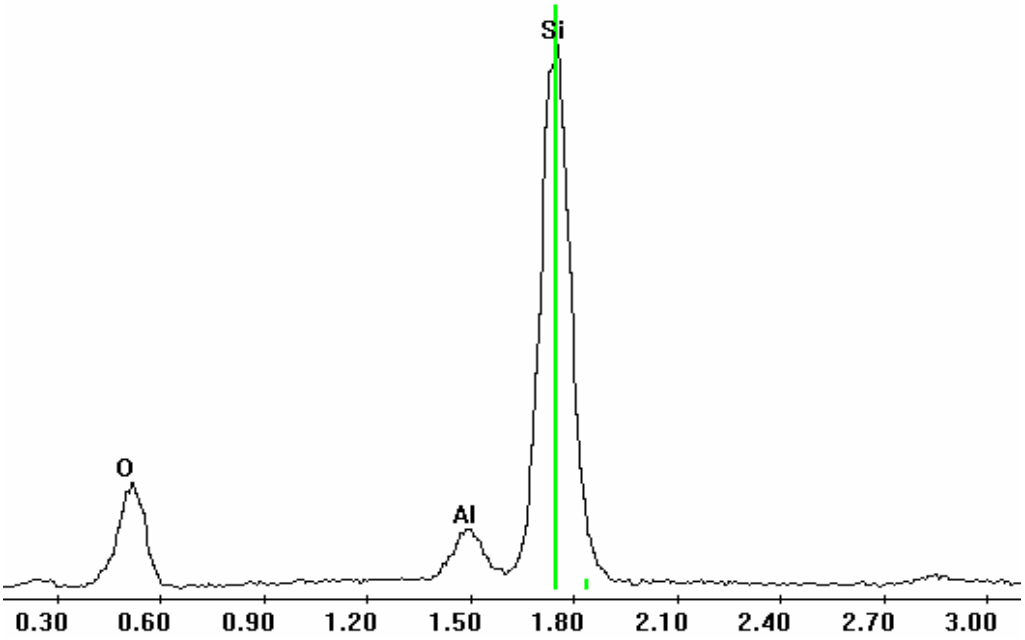



**Figure 19. EDX Spectrum of Mordenite Zeolite Particles**

Pure tungstated zirconia usually appears as clusters of tiny spheres, as shown in Figure 20. (An isolated tungstated zirconia particle in a hybrid catalyst was shown in Figure 17.) The diameter of a single sphere is about two microns. The size of a cluster depends on the number of spheres that stick together and usually ranges from 10 to 20 microns. The mordenite particles are much smaller. Although many of the mordenite particles are in clusters, the size of their agglomerations is usually less than a micron, as shown in Figure 21,

A comparison of the SEM images of a hybrid catalyst (Figure17) with that of a pure tungstate zirconia (Figure 20) and a pure mordenite (Figure 21) shows that PtWZr and mordenite in the hybrid catalyst maintain their individual profiles as before combination.

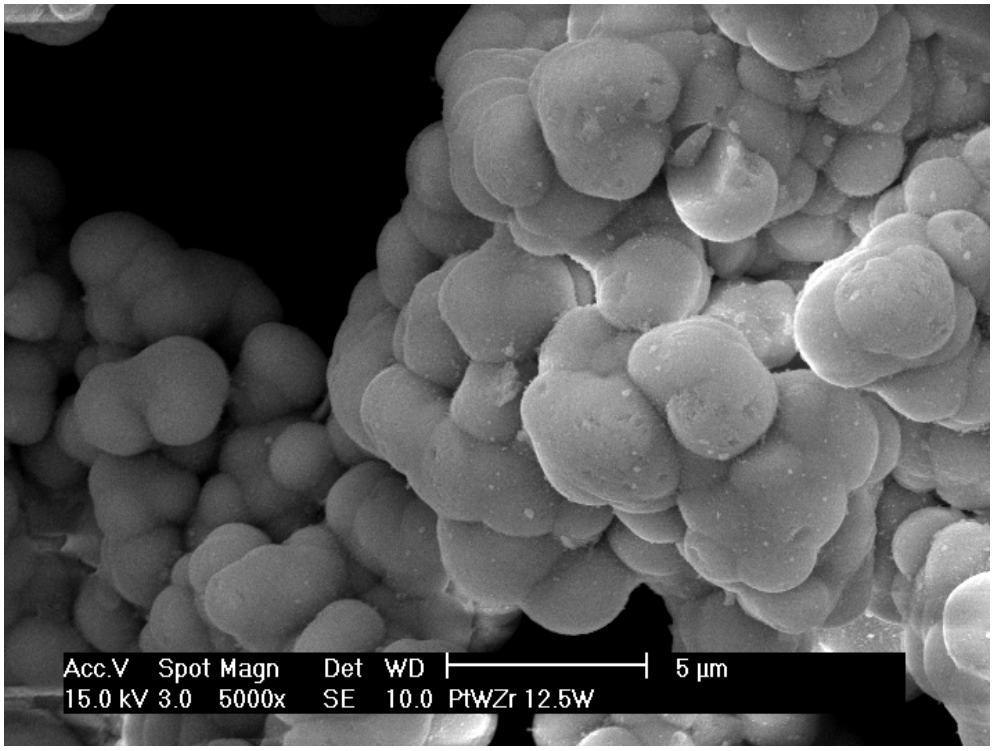



**Figure 20. SEM Image of Pure Tungstated Zirconia Catalyst**

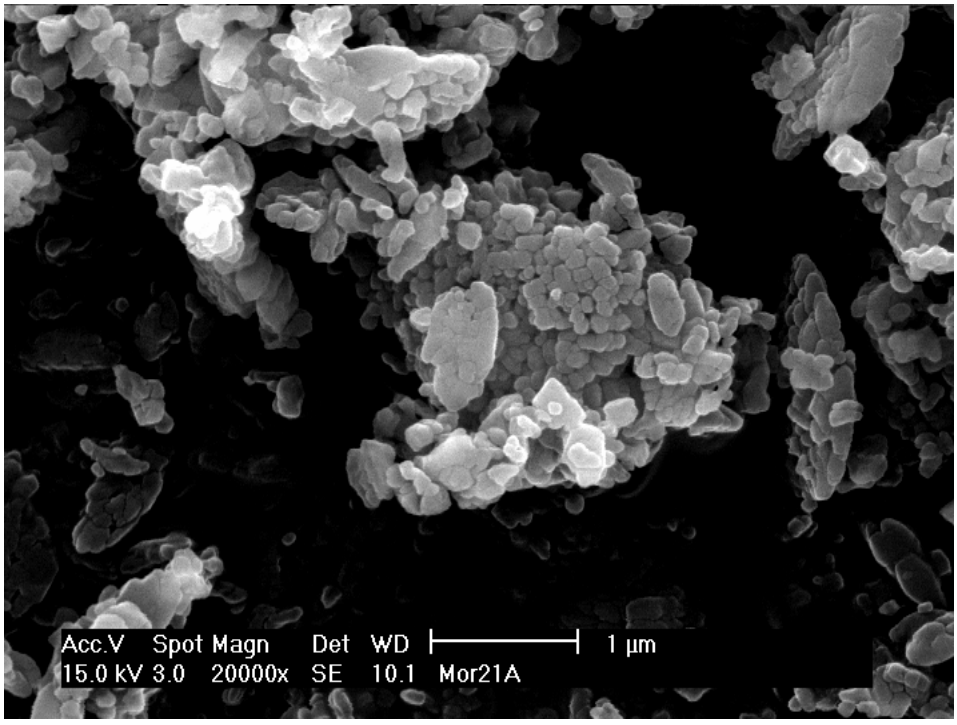
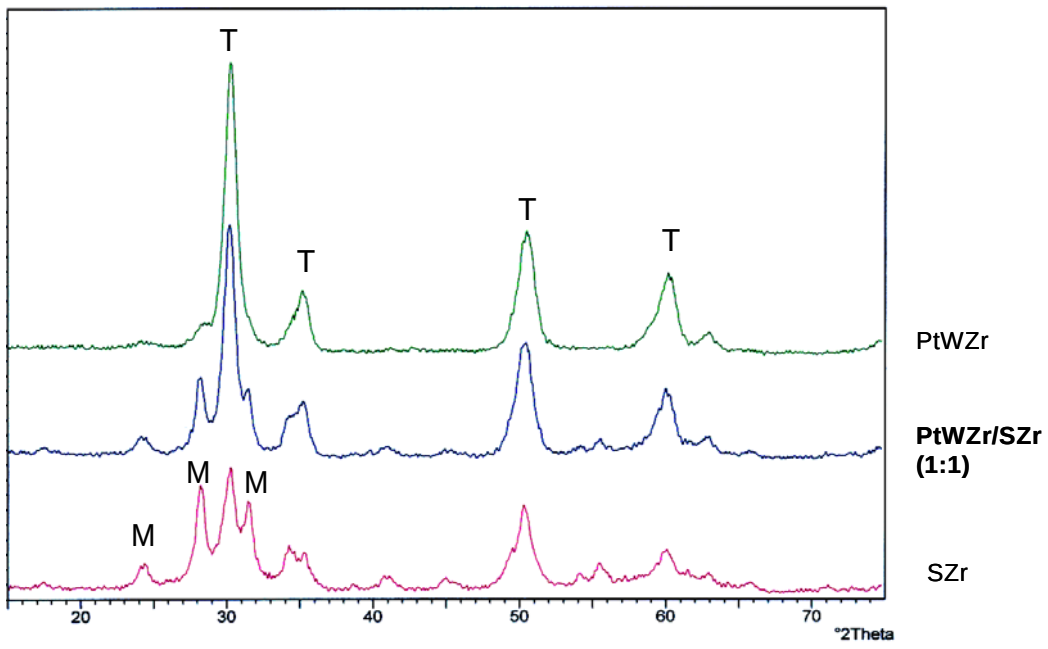



**Figure 21. SEM Image of Pure Mordenite Particles**

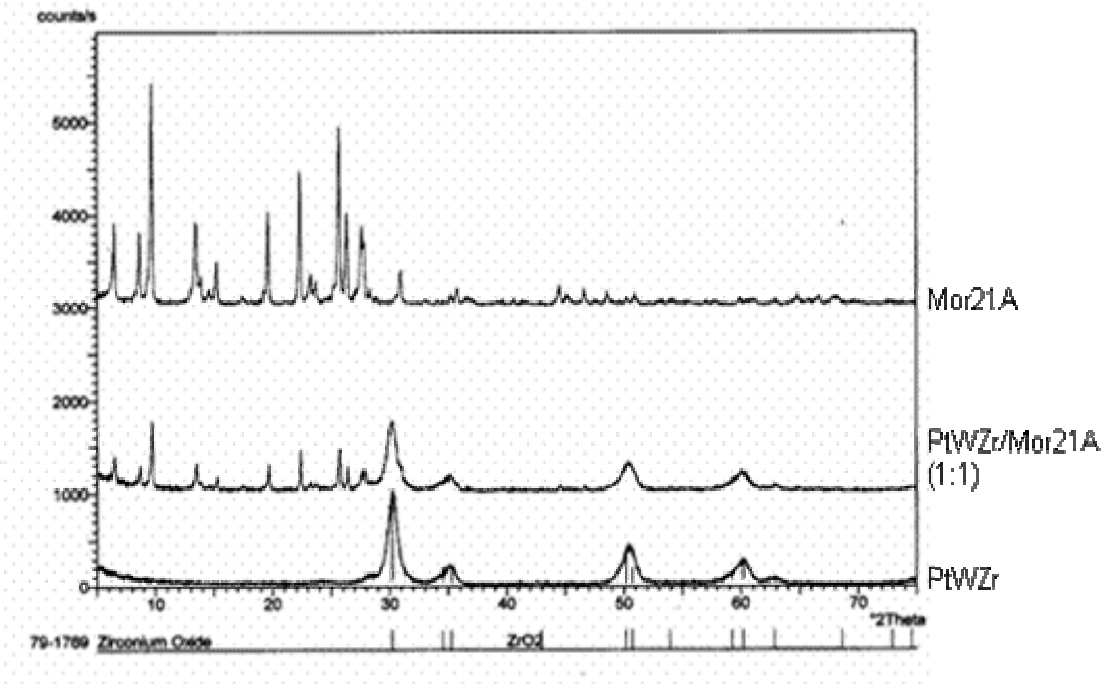
Although there are differences among the various types of zeolites, SEM and EDX analyses of the hybrid catalysts containing these materials suggest that they are mechanical mixtures in close vicinity to each other.

XRD analysis supports the conclusion that the hybrid catalysts are mechanical mixtures. The powder XRD results of hybrid catalysts and their two components before and after combination are shown in Figure 22. The pattern of the hybrid catalyst does not have any new peak that did not exist in the individual components, showing that there is no major change in the crystalline phase as a result of the hybrid combination.




T - Tetragonal zirconia of PtWZr sample
M – Monoclinic zirconia of SZr sample

(A) XRD Patterns of PtWZr/SZr(1:1), PtWZr and SZr




(B) XRD Patterns of PtWZr/Mordenite(1:1), PtWZr and Mordenite

**Figure 22. Powder XRD Analysis of Hybrid Catalysts**

From BET tests, the surface area of a hybrid catalyst is close to the weighted average of the surface area of its components. For example, the BET surface area of a PtWZr/Mor21A(1:1) catalyst is 311 $m^2/g$. Before the combination, the surface area of PtWZr and Mor21A is 103 $m^2/g$ and 550 $m^2/g$, respectively, with a calculated average of 326 $m^2/g$.

5.4.3.2 **Preparation Methods for Hybrid Catalysts** For a hybrid catalyst, various combination methods lead to differences in catalytic performance.

SEM image of PtWZr/Mor21A(1:1) hybrid catalyst synthesized using a "wet-mixing" method, as described in section 4.3.3.1, is shown in Figure 23.

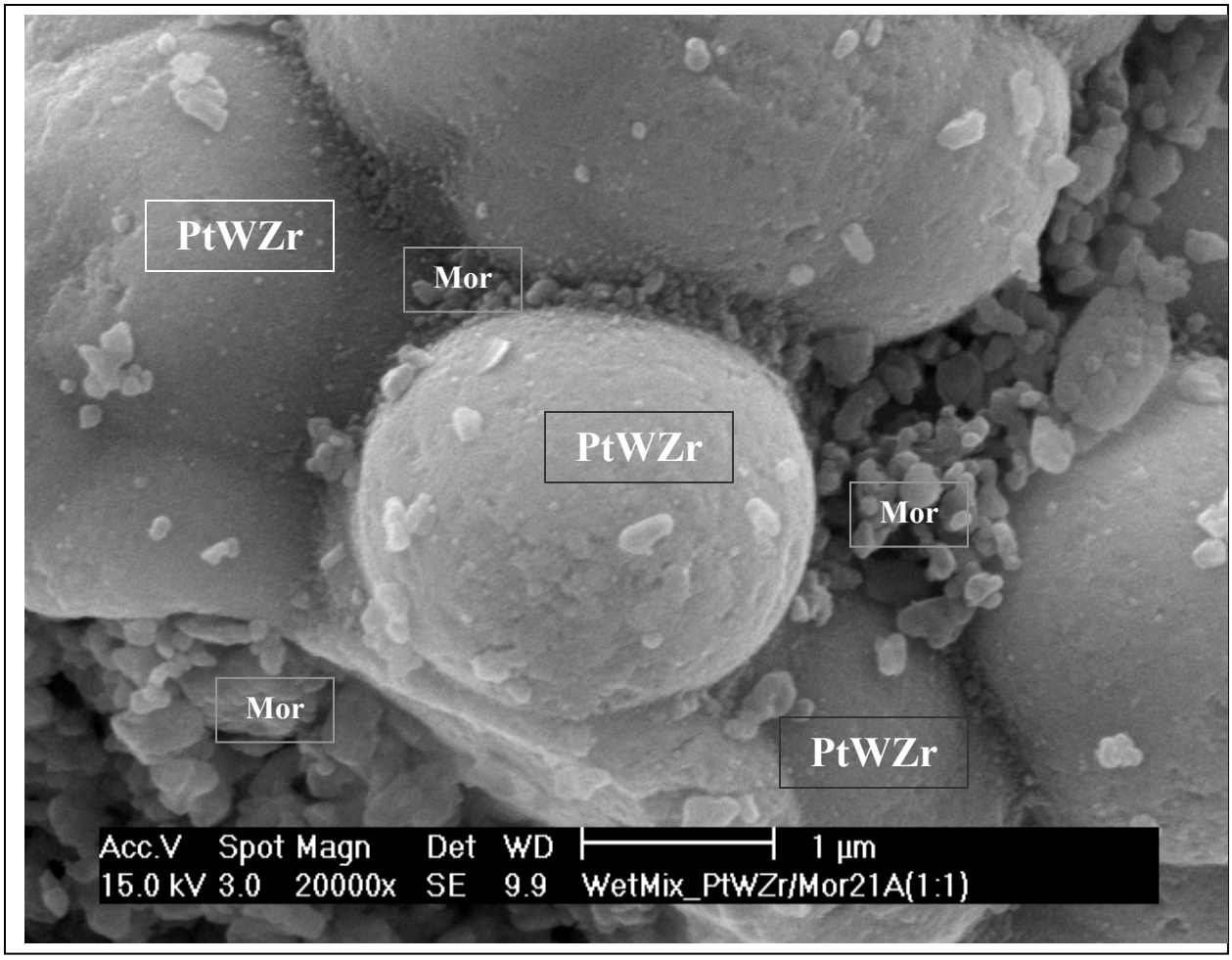



**Figure 23. PtWZr/Mor21A(1:1) Hybrid Catalyst via "Wet-mixing" Method**

The EDX analysis indicates that fine particles of mordenite are scattered around the clustered balls of PtWZr. Compared with Figure 17, where mordenite particles in hybrid catalysts prepared using the "dry-mixing" method stick to each other, mordenite combined with

tungstated zirconia via "wet-mixing" has more isolated particles. Also, because there is no extra grinding involved in "wet-mixing", tungstated zirconia particles are more likely to be in clusters.

As we will see later (Table 13), among all the tested preparation method, "dry-mixing" gave the best hybrid catalysts with good yield to middle distillates. Evidently, the hybrid system prepared via this method gives a configuration that allows the two hybrid components to interact effectively. We used the "dry-mixing" method in preparation of hybrid catalysts further studied in this work.

5.4.3.3 **Combination Ratios** Hybrid catalysts can be prepared with different combination ratios. For a hybrid catalyst containing 0.5 wt% Pt-promoted tungstated zirconia, the introduction of zeolite material not only decreases the Pt concentrations (to be the weighted average concentration), but it also changes the Pt dispersion and Pt surface area. Examples of hybrid catalysts, showing the influence of zeolite components on the Pt conditions of PtWZr components are given in Table 8.

As in Table 8, when the ratio increased from 1:3 to 1:1, the Pt dispersions in PtWZr/Mor21A and in PtWZr/Y720 did not change, but the Pt surface area increased. The hybrid catalysts with a 1:1 ratio had high values for both Pt dispersion and surface area. When there is more of a PtWZr component in the hybrid catalyst, as in a 2:1 ratio, both the Pt dispersion and surface area decrease. The Pt conditions of the hybrid systems are affected not only by the component ratios, but also by the type of the second component. The results of PtWZr/Y zeolite (Table 8) and PtWZr/SZr (Table 9, in section 5.4.3.5) show the effect of component type on the Pt conditions.

**Table 8. Effects of Hybrid Zeolite Components on Pt Dispersion and Surface Area in PtWZr**

| Hybrid Catalyst | Weight Ratio | Overall Pt Concentration, wt% | Pt Dispersion, % | Pt Surface Area, $m^2$/g.Sample |
|---|---|---|---|---|
| PtWZr/Mor21A | 1:3 | 0.13 | 61.7 | 0.19 |
| | 1:1 | 0.25 | 61.8 | 0.38 |
| | 2:1 | 0.33 | 18.9 | 0.15 |
| PtWZr/Y720 | 1:3 | 0.13 | 14.7 | 0.45 |
| | 1:1 | 0.25 | 14.8 | 0.91 |
| | 2:1 | 0.33 | 10.2 | 0.78 |

**5.4.3.4 Acidity of Hybrid Catalysts** We tested catalyst acidities before and after combination to form a hybrid system using TPD with ammonia. The ability to adsorb the basic ammonia molecule are attributed to the acidities of the catalysts. The TPD curve of PtWZr/Mor with 1:1 ratio as well as the curves of pure PtWZr and Mor samples are shown in Figure 24. The acidity of PtWZr/Mor hybrid catalyst is very close to the weight average of the acidities of its components.

The relation of the acidity of PtWZr/SZr hybrid catalysts and the acidities of its components is different than that of PtWZr/Mordenite. As shown in Figure 25, the acidity of PtWZr/SZr differs from the average of PtWZr and SZr.

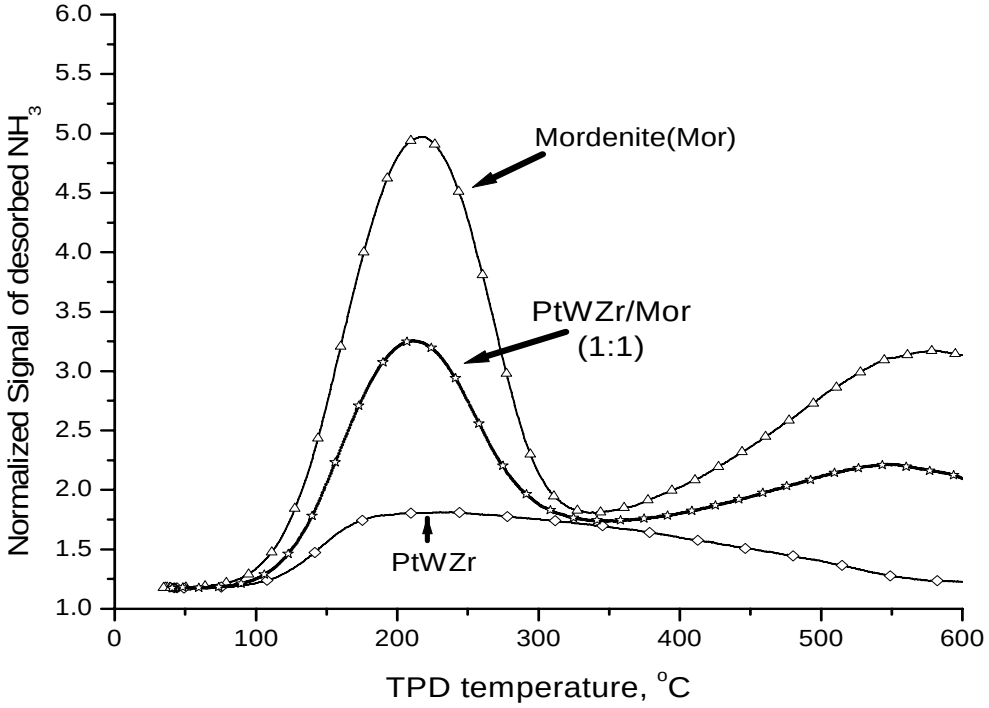



**Figure 24. Acidities of PtWZr/Mor(1:1), PtWZr and Mor (Mordenite)**

5.4.3.5 **Pt Conditions of PtWZr/SZr and PtWZr/PtSZr** The data listed in Table 9 show Pt conditions in PtWZr/SZr hybrid catalysts with different component ratios. The data of PtWZr/PtSZr with 1:1 ratio is also listed for comparison.

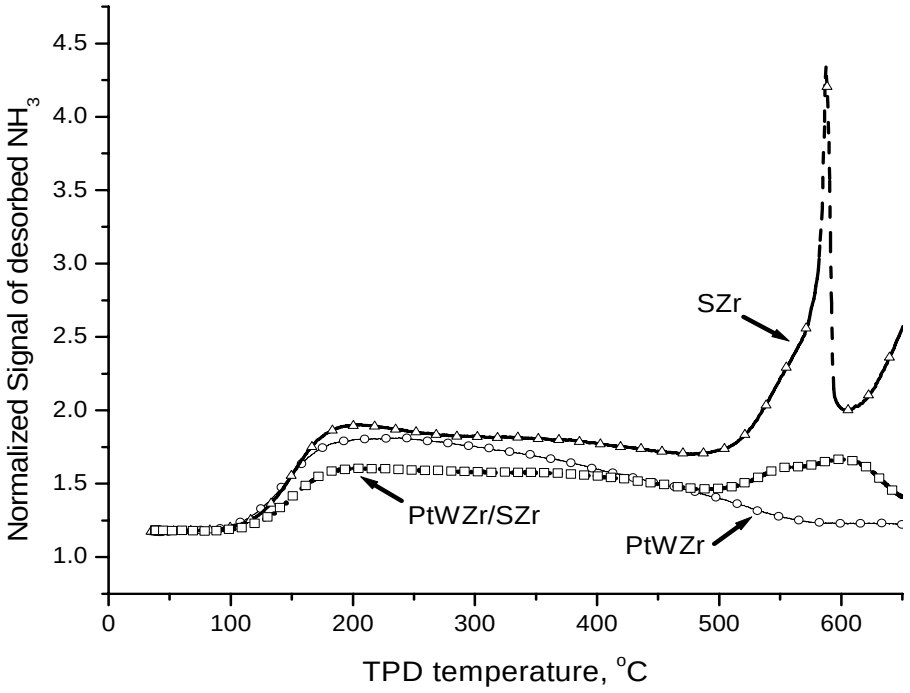



**Figure 25. Acidities of PtWZr/SZr, PtWZr and SZr**

In a PtWZr/PtWZr catalyst, where the SZr component is loaded with Pt, the PtWZr/PtWZr sample has an extremely low Pt dispersion (0.8 %) and Pt surface area (0.011 $m^2$/g.sample), significantly different from PtWZr/SZr or PtWZr/Zeolite samples (Figure 7). As we will see in Table 14, a PtWZr/PtWZr(1:1) catalyst has a much higher cracking function than that of a PtWZr/SZr(1:1) catalyst and the yield of middle distillates is lower, due to extensive cracking leading to production of gasoline. The PtWZr/SZr hybrid catalyst gives higher yield of middle distillates. The Pt conditions of a PtWZr/SZr sample are greatly affected by component ratios. (Table 9). In this research, we used PtWZr/SZr catalysts in studying the application of hybrid catalysts consisting of the two types of anion-modified zirconia catalysts.

**Table 9. Effects of Sulfated Zirconia on Pt Conditions in Hybrid Catalysts**

| Catalyst | Combination Weight Ratio | Average Pt Concentration, wt% | Pt Dispersion, % | Pt Surface Area, $m^2$/g.Sample |
|---|---|---|---|---|
| **PtWZr/SZr** | 1:2 | 0.17 | 40.1 | 0.166 |
| | 1:1 | 0.25 | 43.0 | 0.157 |
| | 3:1 | 0.38 | 12.4 | 0.115 |
| **PtWZr/PtSZr** | 1:1 | 0.5 | 0.8 | 0.011 |

As shown in Figure 26, unlike the grape-like clusters found with tungstated zirconia, sulfated zirconia particles are isolated round balls with rough surfaces. The average size is about 10 microns in diameter. SEM image of particles of a PtWZr/SZr hybrid catalyst is shown in Figure 27. As shown in Figure 18, a PtWZr particle can be identified by EDX showing characteristic peaks of tungsten and zirconium. The EDX spectrum of sulfated zirconia is shown in Figure 28. The characteristic peak of sulfur is small and partly overlaps the zirconium peak. We can confirm that a particle is sulfated zirconia by the absence of major peaks of tungsten.

Based on EDX analysis, the fine particles (marked with "F") covering or contacting the large balls/clusters are also sulfated zirconia components.

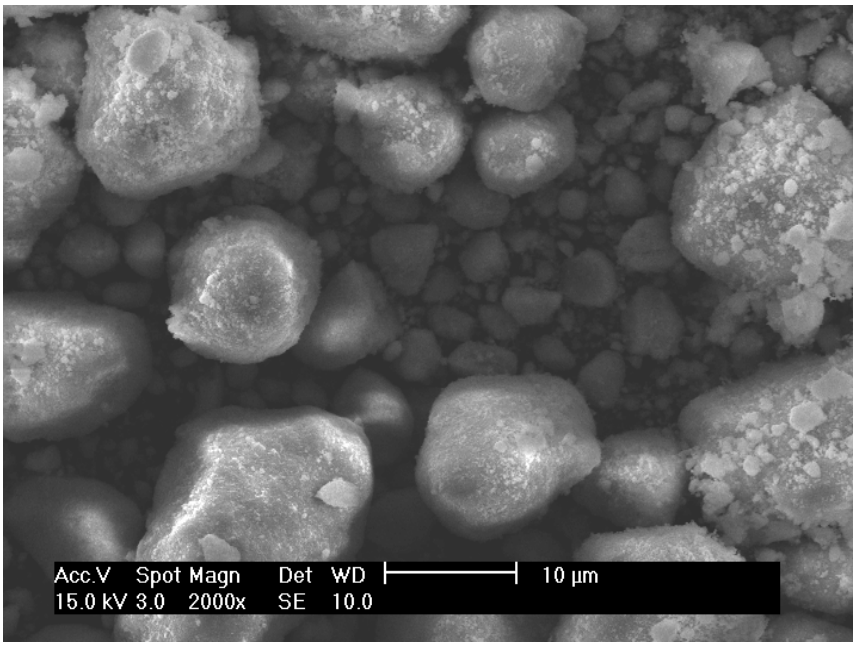
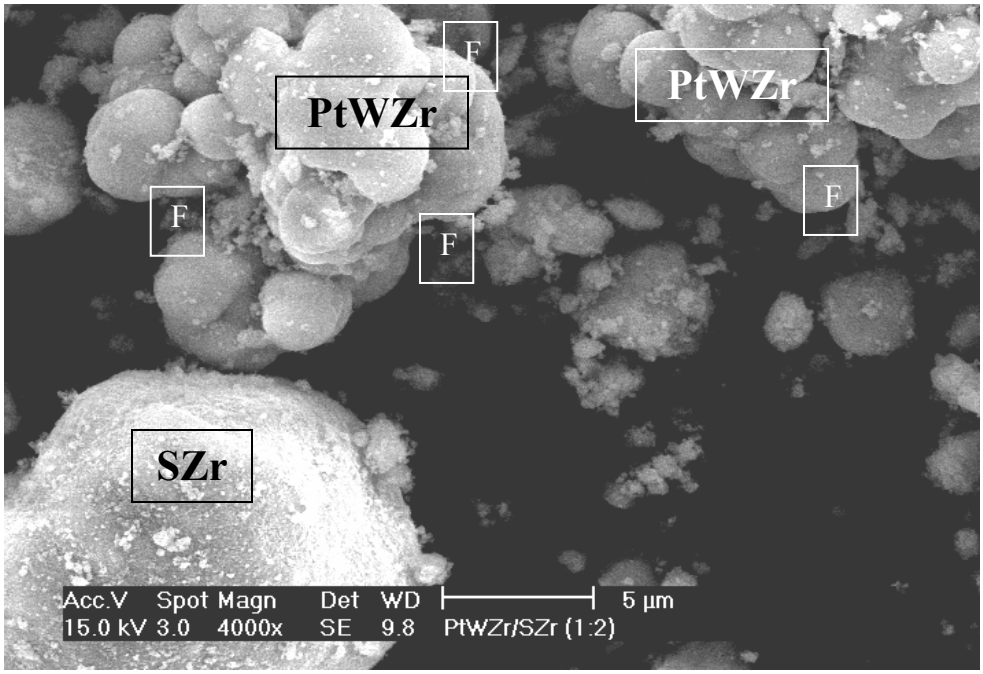



**Figure 26. SEM Image of Sulfated Zirconia Particles**




**Locations marked by "F" indicate fine particles of SZr.**

**Figure 27. SEM Image of PtWZr/SZr Hybrid Catalyst**

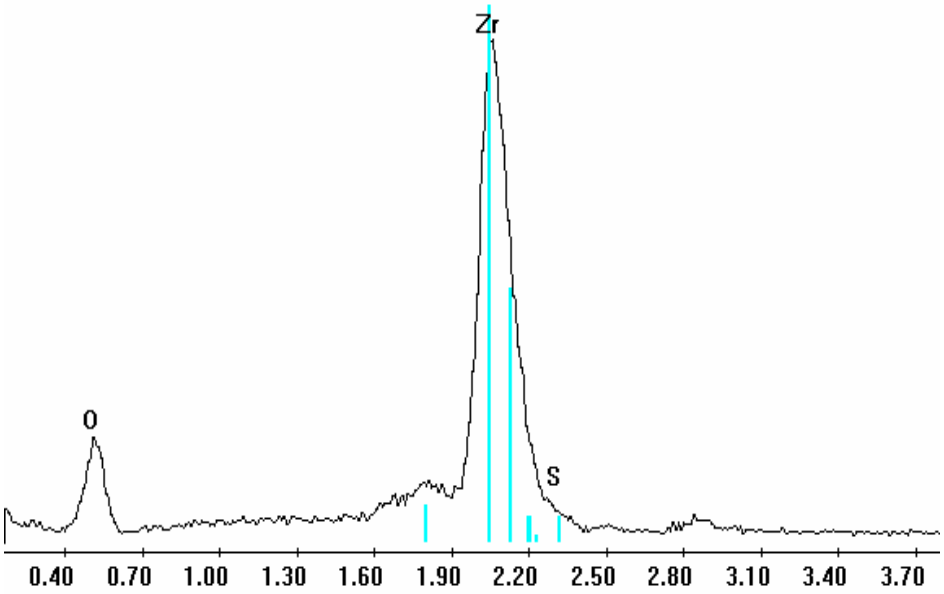



**Figure 28. EDX Spectrum of SZr Catalyst Samples**

As shown in Figure 27, the SZr particles are as large as 10 micron in diameter and most of the PtWZr particles are in the form of clusters. This may be due to the use of only manual grinding in the preparation of hybrid catalysts. Ohyama [(124)] reported that a ball mill can be used in preparing hybrid catalysts. It has been found that long-term milling brought about a lattice disorder (change in XRD patterns) in the hybrid catalyst of CuO and $Cr_2O_3$ as well as smaller particle sizes, enlarged surface areas, which contribute to increased catalytic activity in methanol synthesis.

The results of BET surface area tests support the conclusion that the hybrid catalysts are basically a mechanical combination of its components. The surface area of a hybrid catalyst is close to the weighted average of the surface area of its components. For example, the BET

surface area of a PtWZr/SZr (1:1) catalyst is 133 $m^2/g$. The calculated average of the surface area of PtWZr (103 $m^2/g$) and SZr (175 $m^2/g$) is 139 $m^2/g$.

### 5.4.4 Hybrid Catalysts after Reaction

After some of the reactions, hybrid catalysts were collected and analyzed using XRD and SEM to determine how they were changed by the reaction process. The used catalysts were washed repeatedly using n-pentane to remove any remaining hydrocarbons from the surface. The powder XRD patterns of the catalysts recovered after the reactions were very similar to those of the fresh catalysts. From the SEM image of a hybrid catalyst, it seems that the two hybrid components moved closer to each other after reaction, as shown in Figure 29. For the surface of the used PtWZr/mordenite catalyst, as shown in Figure 30, more areas of the PtWZr surface were covered by a layer of zeolite particles. Some "islands" of PtWZr clusters emerge from the mordenite coverage.

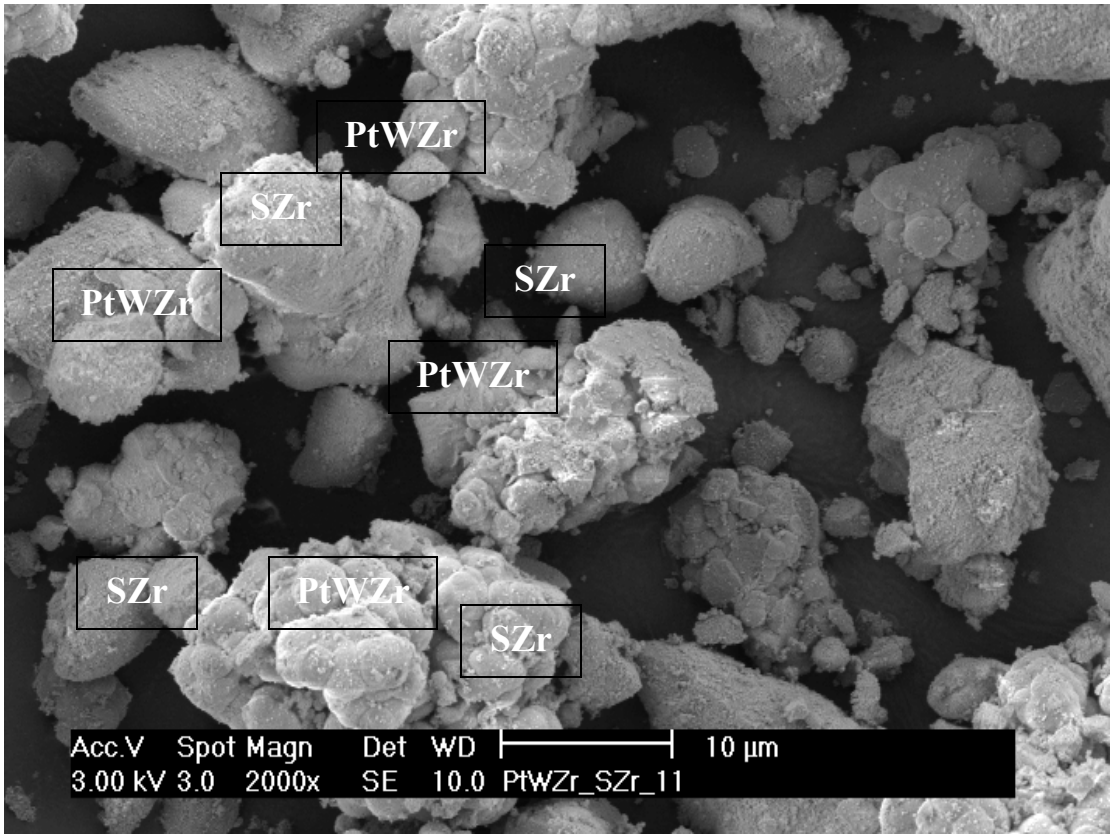
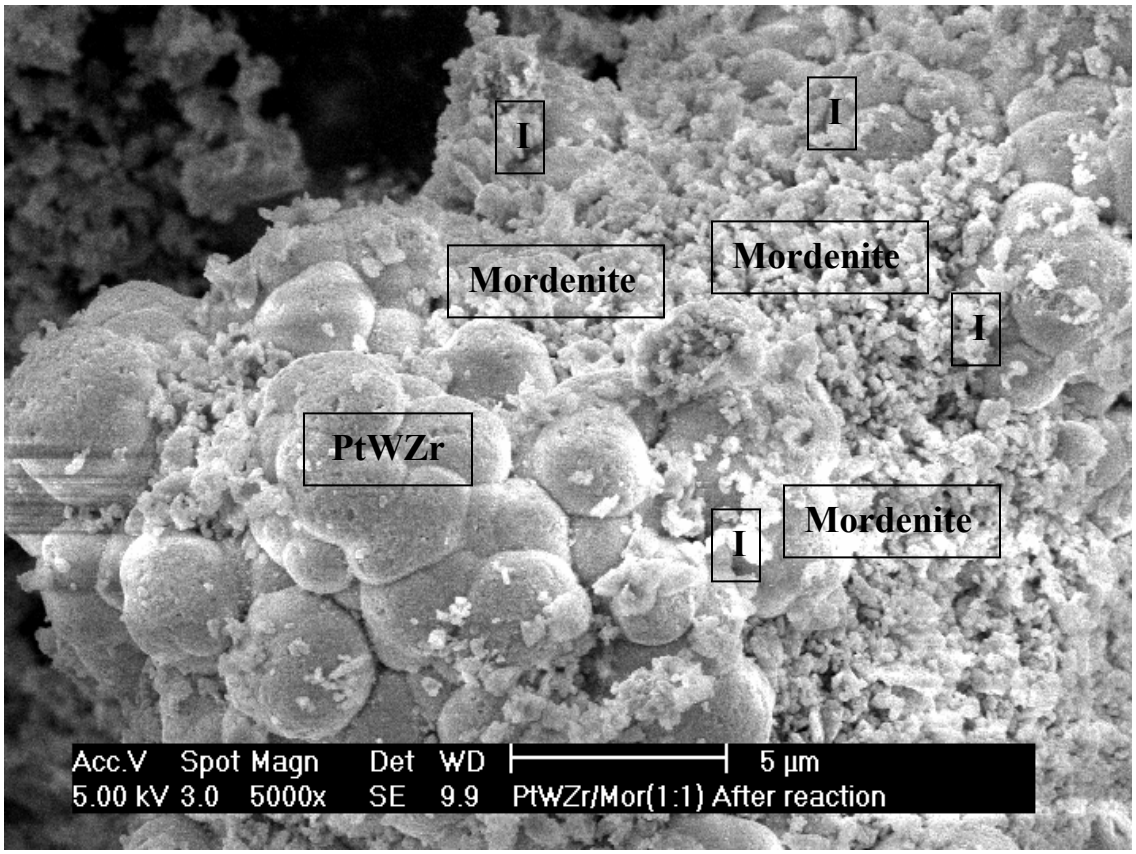



**Figure 29. SEM Image of Used PtWZr/SZr Catalyst**

## 5.5 COMMENTS

The function of Pt is a topic that is under debate. When the Pt concentration is low, the reactivity of a catalyst tends to be very sensitive to Pt conditions and the trend is hard to grasp. [6, 36, 47, 49, 60, 107, 121, 125, 126] In this research, we used a fixed Pt concentration of 0.5 wt% with all catalysts containing a Pt-loading. For PtWZr catalysts, the Pt concentration changes both Pt

dispersion and Pt surface area, the former of which has a greater influence on the reactivity of n-$C_{24}$ conversion. Indeed, with a hybrid catalyst, catalytic performance cannot be predicted by Pt dispersion. PtWZr/WZr (1:1) has similar Pt conditions as PtWZr, but with a much higher yield of $C_{10}$-$C_{20}$ products. Platinum in hybrid catalysts are affected by the component ratio.




**Locations marked by "I" indicate the "islands" of PtWZr.**

**Figure 30. SEM Image of Recovered PtWZr/Mordenite Catalyst after Reaction**

Characterization tests have provided evidence that the hybrid catalysts we prepared are mechanical mixtures of the components. The properties of a hybrid catalyst can be affected by

component ratios and by the methods of preparation. The preparation method affects the dispersion and interaction of the hybrid particles and therefore the catalytic performance. “Dry-mixing” seemed to give hybrid systems an appropriate balance of hydrocracking and hydroisomerization functions for making middle distillates and was adopted for further investigation.

Hybrid catalysts with PtSZr as the second component have extremely low Pt dispersions and surface areas, but have a strong cracking function for gasoline production. We studied mostly PtWZr/SZr catalysts to obtain higher yield of middle distillates.

Although the PtWZr or PtSZr may not be termed superacids, the acidic properties of these two anion-modified zirconia catalysts undoubtedly play a part in determining their reactivity. We used TPD with ammonia ($NH_3$) to determine the acidity of the catalysts. While Pt loading and the high temperature (400°C) hydrogen reduction do not greatly affect the acidity of tungstated zirconia, they decrease the acidity of (Pt-) sulfated zirconia. However, we carried out our work at the relatively low temperature of 200°C, so that the effect of hydrogen reduction was not a big concern.

# 6.0 HYDROISOMERIZATION AND HYDROCRACKING OF LONG-CHAIN HYDROCARBONS USING ANION-MODIFIED ZIRCONIA CATALYSTS

## 6.1 OBJECTIVES

The catalytic behavior of Pt-promoted tungstated zirconia (PtWZr) and sulfated zirconia (PtSZr) catalysts in the hydroisomerization and hydrocracking of long-chain hydrocarbons were investigated. The main objectives of this part of the study were:

(1) To determine and compare the reactivity and selectivity, of the two Pt-promoted anion-modified zirconia catalysts in converting long-chain hydrocarbons to transportation fuels.

(2) To investigate the effects of reaction temperature and hydrogen pressure on the performance of these two types of anion-modified zirconia catalysts.

We used n-$C_{24}$ as the reactant in most of the reactions in this part of research for easier operation and analysis. Study of the two individual catalysts will provide the basis for work with hybrid catalysts. Since n-$C_{36}$ more nearly resembles the hydrocarbons in FT wax, it was used in the study of the effect of hydrogen pressure and in the later study of hybrid catalysts.

## 6.2 BACKGROUND

The hydroisomerization of long-chain normal hydrocarbons, such as n-heptane and n-hexadecane using metal-promoted anion-modified zirconia catalysts have been studied in our laboratories and by other researchers. [5, 24, 26, 29, 53, 55, 61, 93, 98, 127-130] The tungstated zirconia and sulfated zirconia were studied individually and with light molecular weight compounds such as n-butane. Little work has been reported on the use of hybrid systems which combine the functions of the two zirconia catalysts in producing transportation fuels from an FT wax.

## 6.3 EXPERIMENTAL

### 6.3.1 Reaction System

The catalytic tests were carried out in a microautoclave reactor system shown in Figure 31. The effective volume of the reactor (Figure 32) is 27 ml. A Hewlett-Packard (HP) 3421-A data acquisition/control unit was used to control and record the sand bath temperature and to record the internal pressure of the reactor during each experiment.

### 6.3.2 Operating Procedures

In a typical experiment, the catalyst was weighed and activated at 550°C for 90 minutes before being placed into the reactor, which was pre-dried at 110°C overnight. After loading the catalyst, the weighed reactant, i.e. the waxy hydrocarbon, was charged. The reactor was sealed and cooled to room temperature. After loading the reactor, we pressure tested with helium to make sure that there was no leak. After purging with hydrogen three times, the reactor was raised to the desired hydrogen pressure at room temperature. The reactor was then immersed in a fluidized sand bath at reaction temperature and shaken horizontally at 180 rpm during reaction to mix the contents. A computer was used to record the reaction pressure, temperature and time during the run. The reaction was terminated by cooling the reactor with ice water. Reaction variables were reaction time, reaction temperature, hydrocarbon/catalyst ratios and hydrogen pressure. Since we used a batch reactor system, hydrogen pressure changed during reaction because temperature changed and reaction occurred. We report hydrogen pressure as when hydrogen was initially charged at room temperature. Because the cracking reactions consume hydrogen, there were some pressure drops (5 to 30 psi, room temperature) from the initial values when notable cracking happened.

### 6.3.3 Product Analysis

Products in the gas phase were discharged into a collector and analyzed using an HP-6890 gas chromatograph (GC) with an HP Porapak Q 800/100 packed column and a thermal conductivity detector (TCD). Liquid products in the reactor were collected in vials. When waxy products remained in the reactor, appropriate amounts of $CS_2$ were used to dissolve them for

analysis. Liquid samples were injected into a HP-5890 GC, with HP-1 Cross-linked Methyl Silicon Gum, 25m × 0.2mm × 0.33μm column and FID detector. The oven temperature of the GC was increased from 40°C to 320°C at the rate of 5°C per minute. Helium with a flowrate of 50 ml/min was used as the carrier gas. A GC (HP-5890)-MS (HP-5970) was used to identify the structures of the hydrocarbons in the products.

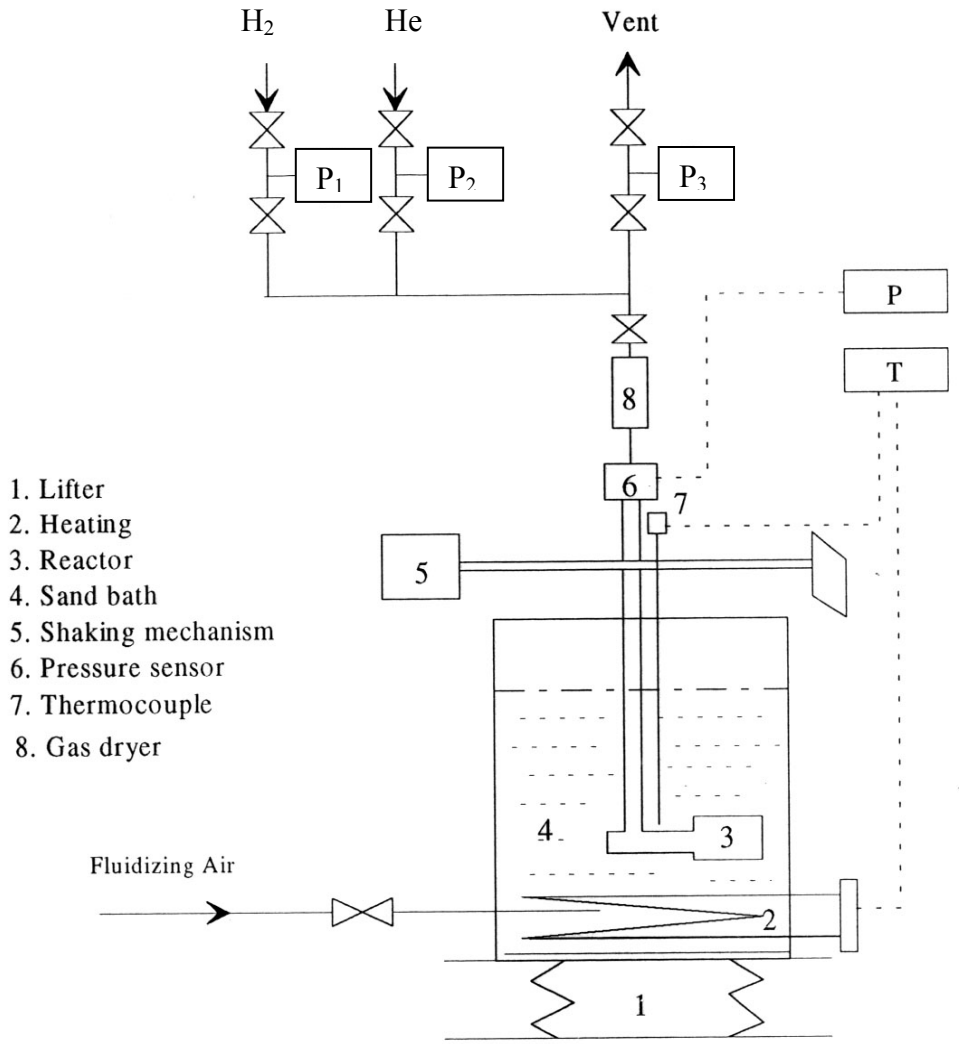



**Figure 31. Diagram of the Reaction System**

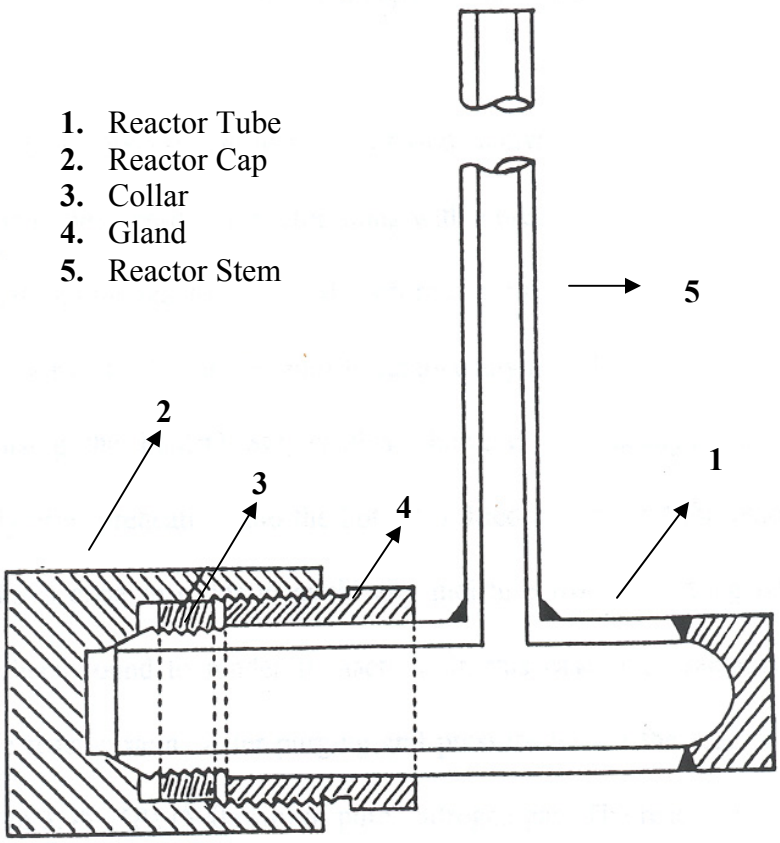



**Figure 32. Structure of the 27 ml Microautoclave Reactor**

## 6.4 RESULTS AND DISCUSSION

There are considerable overlaps in fuel definitions. We grouped our reaction products in the following categories – gasoline, middle distillates and lube-base oils. In the oil industry, a distillate fraction from $C_5$ (boiling point: 25°C) to materials boiling at about 200°C is called gasoline; jet fuel (kerosene) boils from about 200°C to 250°C; the boiling range of diesel is usually from 250-350°C.[95, 131] In this thesis, we name the product ranges by their retention times in GC analysis. Hydrocarbon products ($C_5$ and above) with peaks before that of *n*-$C_9$ (inclusive) are reported as gasoline, products with peaks after *n*-$C_9$, up to and including *n*-$C_{20}$ as middle distillate fuel (including diesel and jet fuel) and products with peaks after *n*-$C_{20}$ as lube-base oil. It is recognized that the lube-base oil product should be highly branched and have a low pour point to be of practical value. A small amount (< 5 wt%) of products lighter than $C_4$ is not reported.

### 6.4.1 Comparison of PtWZr and PtSZr Catalysts

The performances of PtSZr and PtWZr catalysts in converting hydrocarbons are very different. Compared with PtWZr, PtSZr is more active and has much higher selectivity for cracking reactions. There is a large difference in product distributions using these two catalysts

in converting long-chain paraffins. A comparison of their performance with the same degree of conversion was made using n-$C_{24}$ as the reactant.

The product distributions obtained using the two catalysts are shown in Figures 33 and 34. Both reactions are with the same 33 wt% conversion, a temperature of 200ºC and 500 psi hydrogen pressure. Because of its higher reactivity, the PtSZr catalysts need much less catalyst/reactant ratios and shorter reaction time than PtWZr to achieve the same conversion.

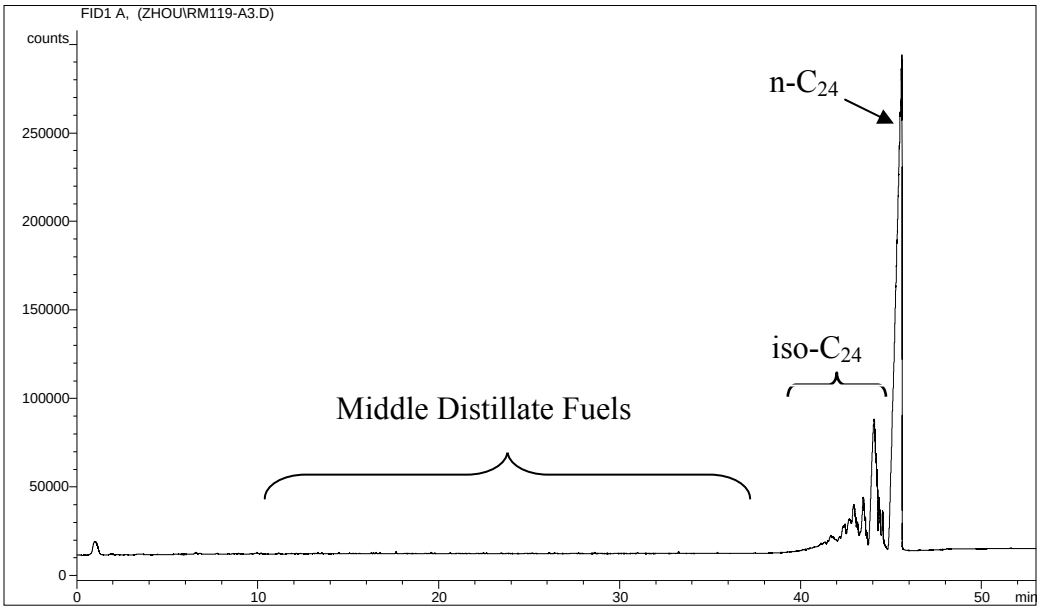



**Figure 33. Product Distribution of Reacted n-$C_{24}$ over PtWZr Catalyst**
(Conversion = 33 wt%, Cata./n-$C_{24}$= 1:4 wt , reaction time=25 min. Run # RM119)

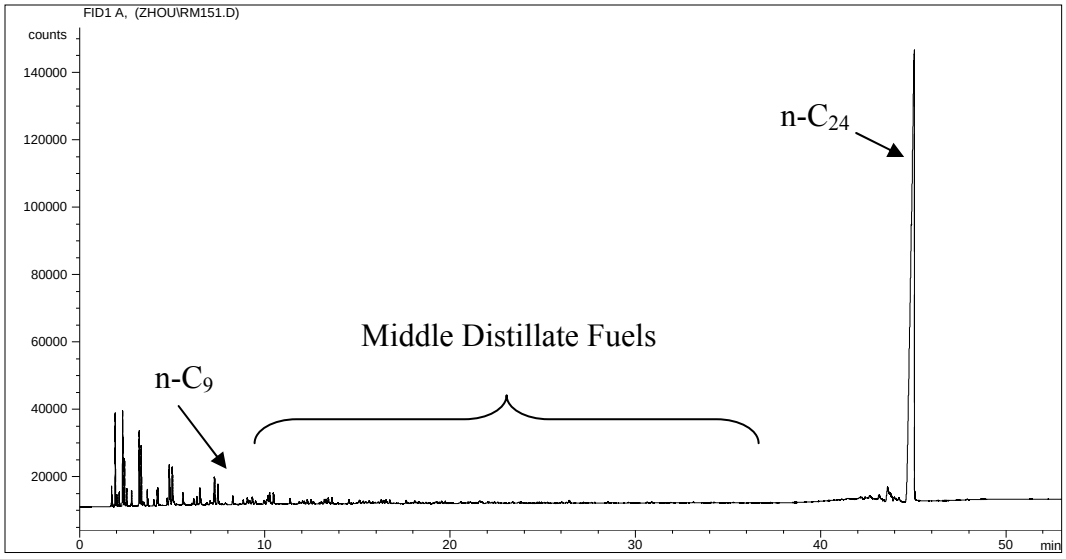



**Figure 34. Product Distribution of Reacted n-$C_{24}$ over PtSZr Catalyst**
(Conversion = 33 wt%, Cata./n-$C_{24}$= 1:12 wt , reaction time=15 min. Run #RM151)

In Figure 33, the main products over PtWZr catalyst are the isomers of $C_{24}$. PtWZr showed good selectivity to hydroisomerization reactions. In Figure 34, a major part of the products consists of hydrocarbons with less than nine carbon atoms. The PtSZr catalyst converts long-chain paraffins to products in the gasoline range even at an early stage of the reaction (conversion of 33 wt%) so that it is not a catalyst for production of middle distillate fuels. The PtWZr catalyst appears to be a catalyst with better potential for producing middle distillates. Although the PtWZr catalyst in Figure 33 does not have a necessary hydrocracking function for high production of middle distillates, its performance can be improved when catalytic components with a cracking function, such as SZr or zeolites, are combined properly with PtWZr. An investigation of this approach will be reported in the next chapter.

The difference in acidities of sulfated and tungstated zirconia catalysts are part of the explanation for their catalytic behavior. Some of the TPD tests for determining the acidities of these catalysts are shown in Figures 12 to 14 and in Figure 24 and 25.

There are other important factors besides acidity that affect the activity of anion-modified zirconia catalysts. For example, some zeolite catalysts, such as mordenite in Figure 24, have a higher acidity than that of PtWZr; but the reactivity of the zeolite is much lower than PtWZr in converting hydrocarbons. As shown in Figure 14, Pt loading decreases the acidity of SZr. However, the activity of SZr is greatly enhanced by Pt, partly because Pt keeps the catalyst surface from deactivation due to coking.

### 6.4.2 Effect of Pt Concentration on PtWZr Reactivity

As discussed in Chapter 2, many theories have been proposed to explain the role of Pt over anion-modified zirconia catalysts, but its role is still not clear. We investigated the effects of Pt concentrations in terms of the dispersion and surface area of Pt over PtWZr. The results are shown in Figure 11. With no Pt, WZr has very low reactivity in converting long-chain paraffins at 200°C. While a small amount of Pt can promote the reactivity of tungstated zirconia, an increase in Pt concentration over 0.25 wt% does not increase its reactivity in converting n-$C_{24}$ or n-$C_{36}$. The results are listed in Table 10. Relating these catalytic results with the data in Figure 11 suggests that the dispersion of the Pt promoter is a better indicator of activity than the surface area.

**Table 10. Effect of Pt Concentration on Reactivity of PtWZr Catalysts**

| Pt concentration, wt % | Reactant | Conversion, wt% |
|---|---|---|
| **0.25** | **n-$C_{24}$** | 50.1 |
| **0.5** | | 41.0 |
| **1.0** | | 25.5 |
| **0.25** | **n-$C_{36}$** | 63.8 |
| **0.5** | | 52.2 |
| **1.0** | | 34.6 |

**Reaction conditions: 200°C, PtWZr: reactant = 1:4 wt, $P_{H2}$= 500 psig, reaction time=25min**

Pt dispersion relates to active metal sites. With 0.25 wt% concentration on the surface of WZr, Pt has the highest (72.5%) dispersion. The presence of abundant active Pt sites is in agreement with its high reactivity.

0.5 wt % is the Pt concentration that has been generally adopted in studying Pt-promoted anion-modified zirconia catalysts. In this research, we used a fixed Pt concentration of 0.5 wt% Pt on all the catalyst with a Pt loading to keep a straightforward comparison.

### 6.4.3 Effect of Reaction Conditions on Catalyst Performance

6.4.3.1 **Effect of Reaction Temperature** Product distribution in catalytic reactions depends on conditions such as reaction temperature, reaction time and the catalyst/reactant ratios. In the present case, higher temperature, longer reaction time and higher catalyst/reactant ratios lead to higher conversions and more cracked products. An increase in reaction temperature from 200°C to 230°C significantly changes the distribution of products (Figure 35. Run#RM077). The conversion of the n-C24 reactant increases from 33 wt% (Figure 33) to 95 wt%. Isomerized $C_{24}$ alkanes are the major products at 200°C. At 230°C, 15 wt% of the product is in the gasoline range and 40.6 wt% of the product is in the middle distillate range.

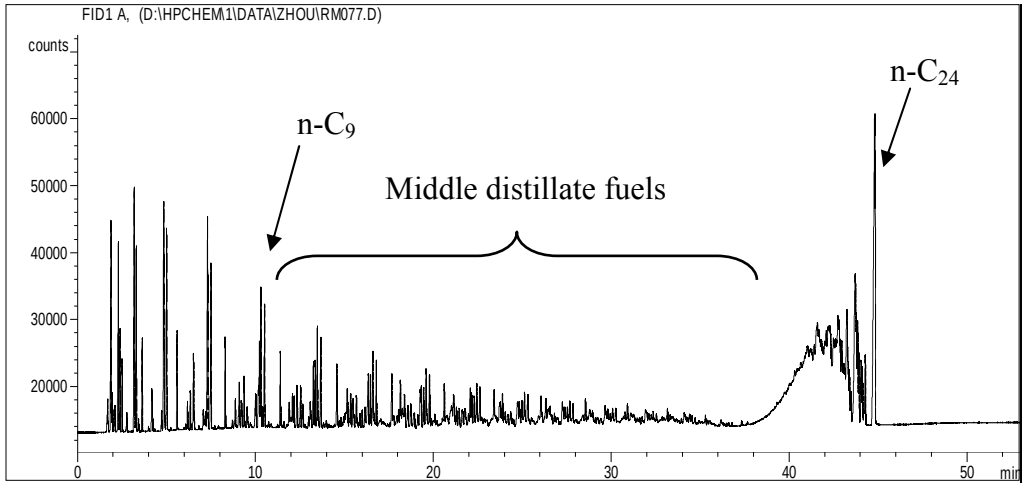



**Figure 35. Higher Temperature (230°C) Leads to Increased Reactivity and Cracking Ability of PtWZr for Producing Middle Distillates**

The majority of the peaks in Figure 35 are due to branched hydrocarbons. Branched products lead to desired properties of transportation fuels. For gasoline, isomerized products have high octane numbers. The properties of a diesel fuel depend not only on its cetane number, but also on its properties at low temperatures. Although the cetane number of isomerized diesel is lower than that of a straight-chain diesel, branched products are desired for the diesel to have good pour-point properties at low temperatures.

The result in Figure 35 shows that reaction conditions such as reaction temperature is one of the many factors that can effectively change product distribution of a PtWZr catalyst. However, in order to compare the catalytic performances of a number of various catalysts, we need to use a set of established reaction conditions as a base. The reaction conditions we used are reaction temperature of 200°C, reaction time of 25 minutes and catalyst/reactant ratio of 1:4 wt. These results will enable further investigations to optimize the catalyst performance by adjusting these reaction conditions. Variables such as reaction temperature make the catalyst system more flexible in the application of various desired products.

6.4.3.2 **Effect of Hydrogen Pressure** We found that temperature, time and catalyst/reactant ratios affect PtSZr and PtWZr catalysts in a similar manner. Higher temperature, longer reaction time and higher catalyst/reactant ratio lead to higher degrees of conversion. Interestingly, hydrogen pressure affects the catalytic performance of the two catalysts in quite different ways in converting long-chain hydrocarbons. For a hybrid catalyst consisting of both PtWZr and SZr, as will be discussed in the next chapter, hydrogen can be very effective in changing the balance of the two components. Studies with n-C36 were used in examining the effects of hydrogen on hybrid catalysts.

### 1) Effect on PtWZr Performance

The reactivity and selectivity of the PtWZr catalyst under two different hydrogen pressures are shown in Table 11. At a hydrogen pressure of 500 psi, use of PtWZr resulted in a 40 wt% conversion of n-$C_{36}$ with high selectivity to isomerized hydrocarbons, 98 wt% of the products are lube-base oil and very little is transportation fuels. At the lower hydrogen pressure of 100 psi, PtWZr has a higher reactivity and conversion increases to 95 wt%. The cracking ability of PtWZr also increased at 100 psi, so that 50 wt% of the product was now in the transportation fuels range, mostly middle distillates.

**Table 11. Effect of Hydrogen Pressure on Reactivity and Selectivity over PtWZr Catalysts**

| Initial $H_2$ Pressure (psi) | Conversion (wt %) | Selectivity (wt %) | | |
|---|---|---|---|---|
| | | Gasoline | Middle Distillates | Lube-base Oil |
| 500 | 40 | 0 | 2 | 98 |
| 100 | 95 | 9 | 41 | 50 |

**Reaction conditions: 0.25 g PtWZr, 1.0 g n-$C_{36}$, 200 °C, 25 min.**

This result is in agreement with other researchers [24-26, 52, 129, 130] who postulated that the PtWZr catalyst has a high hydrogen transfer rate and therefore a low surface residence time of carbenium ions. As shown in Figure 36[52], PtWZr catalyzes hydrogen dissociation and provides hydrogen atoms required for hydrogen transfer and carbenium desorption steps. The rapid hydrogen transfer on PtWZr leads to fast neutralization and desorption of carbenium ions, so that extensive cracking of adsorbed carbenium ion is prevented. The quasi-equilibrated hydrogen

transfer steps leads to short surface lifetimes and low steady-state carbenium coverage. With high hydrogen pressure, the competitive binding of $H^+$ and carbenium ions on the catalysts surface decreases the surface density of carbenium ions so that the reactivity is lower. [26] Zhang et al. studied n-$C_{16}$ isomerization and also observed a negative reaction order with respect to hydrogen.[53]

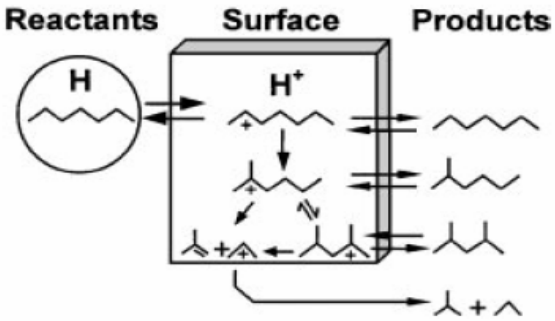
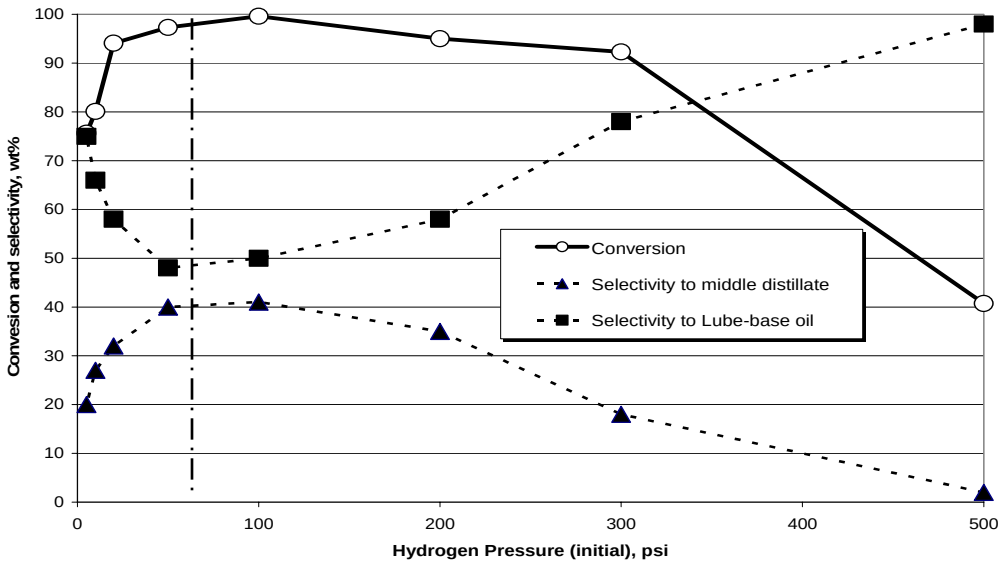



**Figure 36. Scheme of n-Heptane Isomerization on PtWZr**

PtWZr catalysts were tested with a series of hydrogen pressures. As shown in Figure 37, a highest reactivity and selectivity to middle distillate fuels were obtained with a hydrogen pressure near 100 psi. The conversion declines above 100 psi, suggesting a negative order of hydrogen pressure; reactivities also decrease below 100 psi hydrogen pressure, which is attributable to catalyst deactivation caused by insufficient hydrogen. In both stages, selectivity to middle distillates changes together with conversion, showing that higher reactivity of PtWZr always favors higher selectivity of middle distillate within the tested pressure range. We also found that it is the hydrogen partial pressure and not the total pressure that determines the

performance of the catalysts. Charging an additional 450 psi of argon to 50 psi hydrogen did not significantly change the reactivity and selectivity.




Reaction conditions: 0.25 g PtWZr, 1.0 g n-$C_{36,}$ 200 °C, 25 min. Data listed in Table 16.

**Figure 37. Effect of Hydrogen Pressure on Converting of n-$C_{36}$ Using PtWZr Catalysts**

**2) Effect on the PtSZr Catalyst**

The PtSZr catalyst responds to a change of hydrogen pressure (as shown in Table 12) in a different way than with PtWZr. At a hydrogen pressure of 500 psi, PtSZr showed a higher reactivity with a greatly increased conversion (95 wt %). The cracking function of PtSZr was so strong under high hydrogen pressure that major products were found in the gasoline range (65 wt %); the 20 wt% selectivity to the middle distillate fuel range was lower than that under 100 psi hydrogen pressure. The higher reactivity of PtSZr does not give good selectivity to middle distillate products.

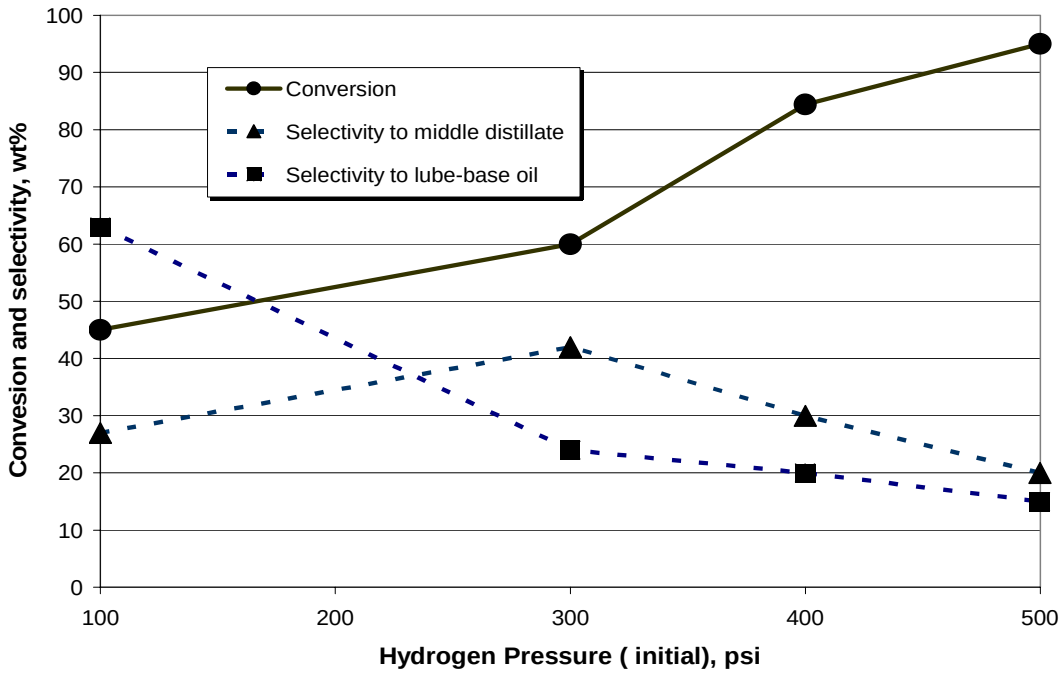
Different effects of hydrogen on sulfated zirconia catalysts have been reported in the isomerization of short chain paraffins, such as n-butane. Garin et al. [105] found higher hydrogen pressure led to high reactivity and attributed it to the activation of Pt. Liu and Sachtler found that increased hydrogen pressure resulted in decreased reactivity of PtSZr in butane isomerization [132] and explained it by postulating an olefin intermediate. However, olefinic species may not be the key intermediates in the hydroisomerization and hydrocracking of longer-chain paraffins, such as n-$C_7$ and n-$C_{16}$. [55, 58, 133] Some conclusions for short-chain paraffin hydroisomerization are not applicable to long-chain reactants, which crack more easily[5, 6, 134-137] . The positive effect of hydrogen pressure found on the reactivity of the PtSZr catalyst in converting n-$C_{36}$ supports the view that an olefinic intermediate may not be involved in the reactions; higher hydrogen pressure makes it harder to generate an olefinic intermediate.

**Table 12. Effect of Hydrogen Pressure on Reactivity and Selectivity over PtSZr Catalysts**

| Initial $H_2$ Pressure (psi) | Conversion (wt%) | Selectivity (wt %) | | |
|---|---|---|---|---|
| | | Gasoline | Middle Distillates | Lube-base Oil |
| 100 | 45 | 10 | 27 | 63 |
| 500 | 95 | 65 | 20 | 15 |

**Catalyst: 0.2 g PtSZr Reactant: 0.8 g n-$C_{36}$ Reaction conditions: 200 °C, 20 min.**

The conversion and selectivity of PtSZr under hydrogen pressures from 100 psi to 500 psi is shown in Figure 38. With higher hydrogen pressure, the reactivity of PtSZr increases and conversion increases accordingly. At around 300 psi, the selectivity to middle distillate products starts to decrease. The reactivity and cracking capability of PtSZr is very strong under high hydrogen pressures, so that extensive hydrocracking reactions occur and more light products, in the gasoline range, are produced. This is different from the case of PtWZr. Because PtWZr does not have a strong cracking capability, its selectivity to gasoline is kept low (9 wt %) even with a high conversion of 95 wt%.




Catalyst: 0.2 g PtSZr, Reactant: 0.8 g n-$C_{36}$ Reaction conditions: 200 °C, 20 min.
Data listed in Table 16.

**Figure 38. Effect of Hydrogen Pressure on Hydrocracking of n-$C_{36}$ Using PtSZr Catalysts**

# 7.0 HYBRID CATALYSTS FOR HIGHER YIELDS OF MIDDLE DISTILLATES

## 7.1 OBJECTIVES

As shown in Figures 33 and 34, PtWZr and PtSZr demonstrate different features in converting long-chain alkanes. Each of these catalysts can be used to produce products in the lube-base oil or gasoline range, but conversion of long-chain FT hydrocarbons with high yields of middle distillates is more challenging. In this part of study, we intended to build a catalytic system termed as "hybrid catalysts" that combines the special hydrocracking and hydroisomerization functions of the two catalyst components for increased yields of middle distillates. Various factors of the hybrid catalyst systems were studied to evaluate their influence on reactivities and selectivities. Those factors included preparation methods, types of the hybrid component and component ratios. As an important variable that affects PtWZr and PtSZr in different ways, hydrogen pressure was to be studied in changing the balance of the two types of anion-modified zirconia components in the hybrid system.

The hybrid catalysts we obtained are flexible in producing various desired products. The product distributions are affected by reaction conditions such as temperature, time and hydrogen pressure. In order to review and compare the performance of a number of catalyst systems, we must carry out the experiments with a set of established conditions. We used conditions such as 200°C, a 25-minute reaction time and 1:4 catalyst/reactant ratio as base conditions. The results

from this study will furnish a foundation for further investigations. Other reaction conditions and variables can be utilized to exploit the flexibility and full potential of the catalysts.

## 7.2 EXPERIMENTAL

Catalytic testing of hybrid catalysts was carried out on the same microautoclave reaction system used when studying the PtWZr and PtSZr catalysts. The operating procedures and product analyses are discussed in Chapter 6. For a better representation of the heavy hydrocarbons as found in FT waxes, we used n-$C_{36}$ as the model reactant.

## 7.3 RESULTS AND DISCUSSION

Two types of hybrid catalyst systems have been prepared and tested in this work. One is the hybrid catalysts consisting of Pt-promoted tungstated zirconia (PtWZr) and sulfated zirconia (SZr) catalysts; the other is the hybrid catalysts consisting of PtWZr and a zeolite component.

### 7.3.1 Hybrid Catalysts Consisting of PtWZr and SZr

PtWZr and PtSZr have been studied as individual catalyst in hydroisomerization and hydrocracking of hydrocarbons. To the best of our knowledge, there is no report on the study of combining the functions of these two zirconia catalysts for improving performance in converting long-chain alkanes. We once prepared $Pt/SO_4^{2-}/WO_3/ZrO_2$ catalyst by doping WZr sample in sulfuric acid solution follow by Pt loading. But the catalyst was not reactive in converting n-$C_{36}$. There are reports[41, 62, 63, 68, 124, 138-140] about mechanical mixtures (hybrid catalysts) combining the functions of their components for improved catalytic performance. We found that the functions of the two anion-modified zirconias actively interact in some hybrid catalyst systems we prepared. Before mixing, the two catalysts were each prepared and their activities examined.

**7.3.1.1 Effective Preparation Method for Active Hybrid Catalysts** Three different mixing methods for preparing hybrid catalysts were described in Chapter 4. Following these methods, hybrid catalysts consisting of PtWZr and SZr as the second component were prepared. A comparison of reactivities and selectivities for n-C36 conversion using PtWZr/SZr prepared by different methods are shown in Table 13. The component weight ratio of 1:1 wt was chosen for comparison. The hybrid catalysts synthesized via the "Dry-mixing" method gave the highest reactivity and cracking selectivity for middle distillate transportation fuel products.

According to SEM and EDX analysis of hybrid catalyst samples, the PtWZr and SZr particles stick rather closely to each other. (Figure 27). The catalysts prepared via different methods lead to different vicinities and contacts among the particles, resulting in different catalytic performance. In a hybrid catalyst prepared by the "wet-mixing" method, as in

Figure 23, the arrangement of particles of the two components is different from that in a "dry-mixing" case, as shown in Figure 17. The different ways in which hybrid particles contact each other should affect their contribution in the hybrid system. A comparison of the performance of hybrid catalysts prepared via different methods is shown in Table 13. Since hybrid catalysts prepared by the "Dry-mixing" method has the higher reactivity than other tested preparation methods, we prepared all the hybrid systems in this way. There are also reports about obtaining active mixtures using a binder[62] or a ball mill[124], which were not used in this work.

Detailed discussion about the characteristic analysis of these hybrid catalysts are reviewed in Chapter 5.

**Table 13. Preparation Methods Affect the Performance of Hybrid Catalysts**

| Catalyst | | Conversion (wt %) | Selectivity, (wt%) | | |
|---|---|---|---|---|---|
| | | | Gasoline | Middle Distillates | Lube-base Oil |
| PtWZr | | 92 | 4 | 16 | 80 |
| PtWZr/ SZr (1:1 wt) | Direct Addition | 30 | 3 | 12 | 85 |
| | Wet-mixing | 26 | 2 | 7 | 91 |
| | Dry-mixing | 93 | 18 | 45 | 37 |

**Temperature= 200 °C; $P_{H2}$= 300 psig; Reaction time = 25 min; 0.25 g Catalyst/1.0g n-$C_{36}$**

The product distribution using a PtWZr/SZr (1:1) is shown in Figure 39 (Run# R277-2). Compared with the typical product distributions of PtWZr and PtSZr catalysts, as in Figures 33 and 34, enhancement in yield of middle distillates using the hybrid catalyst is significant.

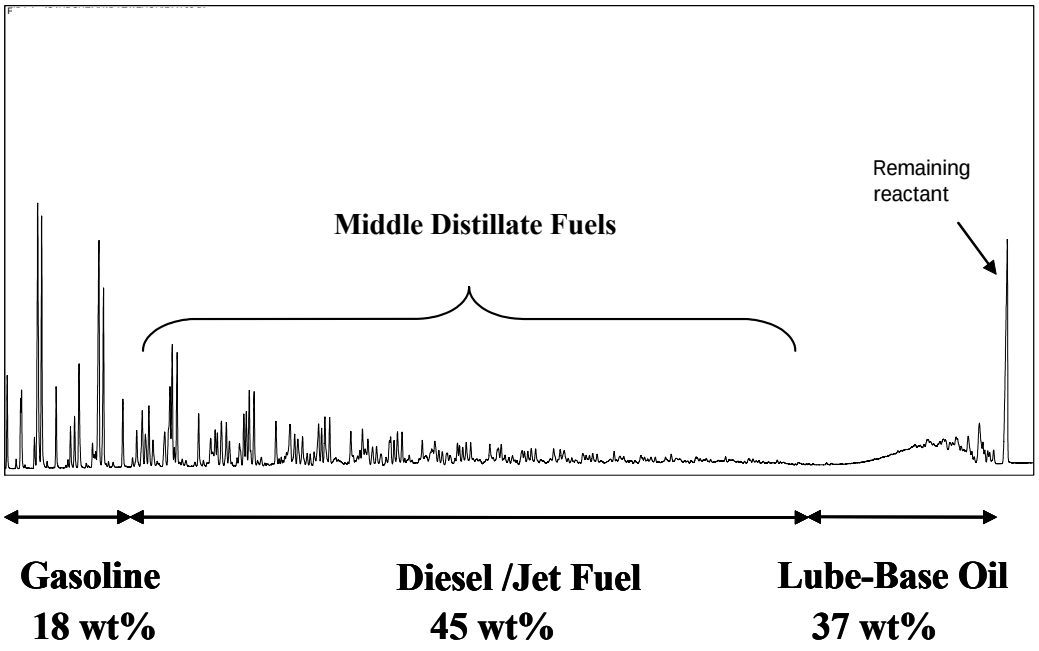



**Figure 39. Product Distribution of Converted n-$C_{36}$ Using PtWZr/SZr(1:1) Hybrid Catalysts**

7.3.1.2 **Effect of Pt loading** Pt loading is very important for the anion-modified zirconia catalysts to have stable reactivities. Without Pt, WZr/SZr is not active enough in conversion of n-C36. However, when Pt is directly loaded on the SZr component, the hybrid catalysts has too strong a hydrocracking function to obtain high yields of middle distillates, as shown in Table 14.

CO chemisorption in Chapter 5 measures the Pt conditions on the catalyst. For a PtWZr sample with 0.5 wt% Pt, the Pt dispersion and surface area were 58wt% and 0.727

$m^2$/(g.sample), respectively. After PtWZr and PtSZr were combined, the Pt dispersion and surface area of the hybrid catalyst dropped to 0.8 % and 0.011 $m^2$/(g.sample), respectively. The PtWZr/PtSZr catalyst has strong reactivity and cracks the reactant into gasoline product. Compared to this, the PtWZr/SZr hybrid catalyst made of a 1:1 ratio of PtWZr and SZr (without Pt loading on the SZr) had a high Pt dispersion (43%) as well as a high yield of middle distillates. (Table 13)

Pt dispersion and surface area are not the only factors that are related to the performance of the hybrid catalyst system. PtWZr catalyst has Pt dispersion and surface area higher than that of a PtWZr/SZr (1:1) catalyst, but has a much lower reactivity and yield of the desired middle range products from n-$C_{36}$**.**

**Table 14. Pt Conditions over Hybrid Catalysts Containing Sulfated Zirconia**

| Catalyst | Pt Disp., % | Pt Surface Area, $m^2$/g.Sample | n-$C_{36}$ Conv., wt% | Selectivity, wt% | | |
|---|---|---|---|---|---|---|
| | | | | Gasoline | Middle Distillates | Lube-base oil |
| **PtWZr** | 58.8 | 0.727 | 92 | 4 | 16 | 80 |
| **PtWZr/ PtSZr (1:1)** | 0.8 | 0.011 | 95 | 88 | 8 | 4 |
| **PtWZr/ SZr (1:1)** | 43 | 0.157 | 93 | 18 | 45 | 37 |

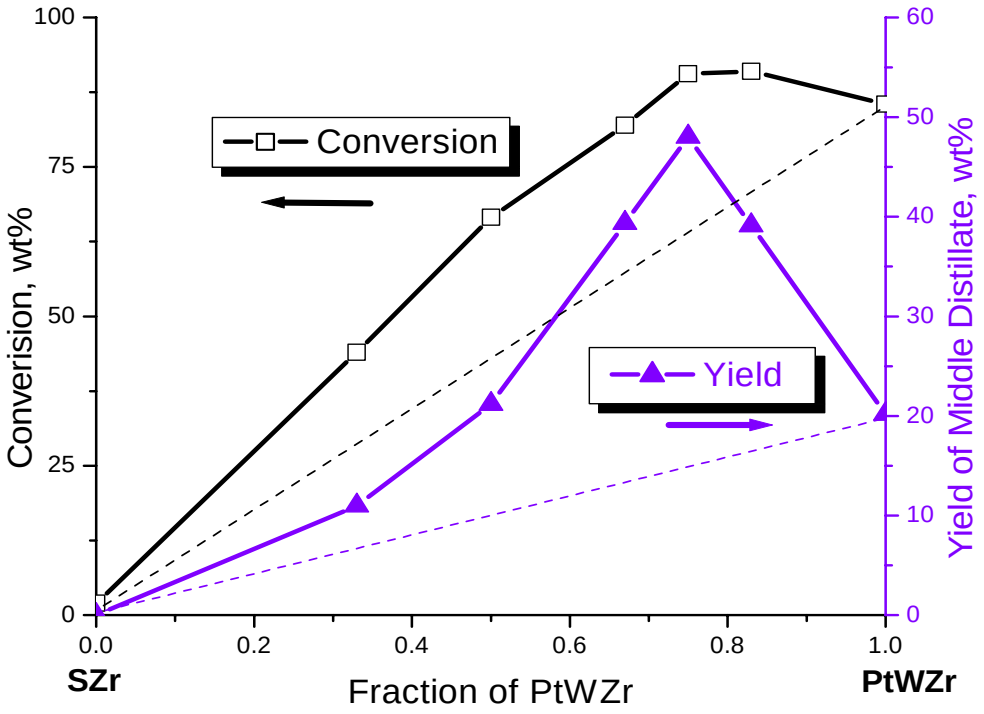
**Reaction conditions: 200 °C, 25 min, catalyst/n-$C_{36}$ = 1:4 wt, $P_{H2}$=300 psig**

7.3.1.3 **Effect of Component Ratio on Hybrid Catalyst Performance** As shown in Figure 39, the reactivity and selectivity of PtWZr/SZr hybrid catalysts are affected by the component ratio. With a hydrogen pressure of 100 psig, pure PtWZr catalyst has good activity (40 wt % n-C36 conversion) but low selectivity to middle distillate, likely due to lack of sufficient cracking capability. The introduction of the cracking function of the SZr component significantly increased the yield of middle distillates. With a hybrid catalyst consisting of PtWZr/SZr (3:1), where 25wt% of PtWZr was replaced by SZr, the increased cracking ability led to a significant improvement in the yield to middle distillate products. The conversion was also increased and was significantly higher than the weighted average conversion of the two components. It suggests an active interaction between the hybrid components.

From the results shown in Figure 40, in a PtWZr/SZr hybrid catalyst, both the PtWZr and the SZr component contribute to the system. Without direct Pt loading, SZr alone is not reactive. The fact that SZr component demonstrates its contribution in the hybrid catalyst means that the combination with the PtWZr component helps to keep SZr from deactivation and maintain its reactivity. SZr in the PtWZr/SZr system does not have high cracking functions as in PtSZr, so that n-$C_{36}$ is not extensively converted to a gasoline-type product.

The component ratio effectively changes the balance between the functions of the hybrid components. Under a given condition, an optimum component ratio exists for an appropriate balance between isomerization and cracking for converting n-$C_{36}$ to middle distillates. With that optimum ratio, in this case about 3:1 PtWZr/SZr, a maximum yield of middle distillate products

of about 50 wt% can be achieved. Figure 40 shows the results of catalyst comparison under the given reaction conditions, which may not be the optimum conditions to obtain the highest possible yield of middle distillates.



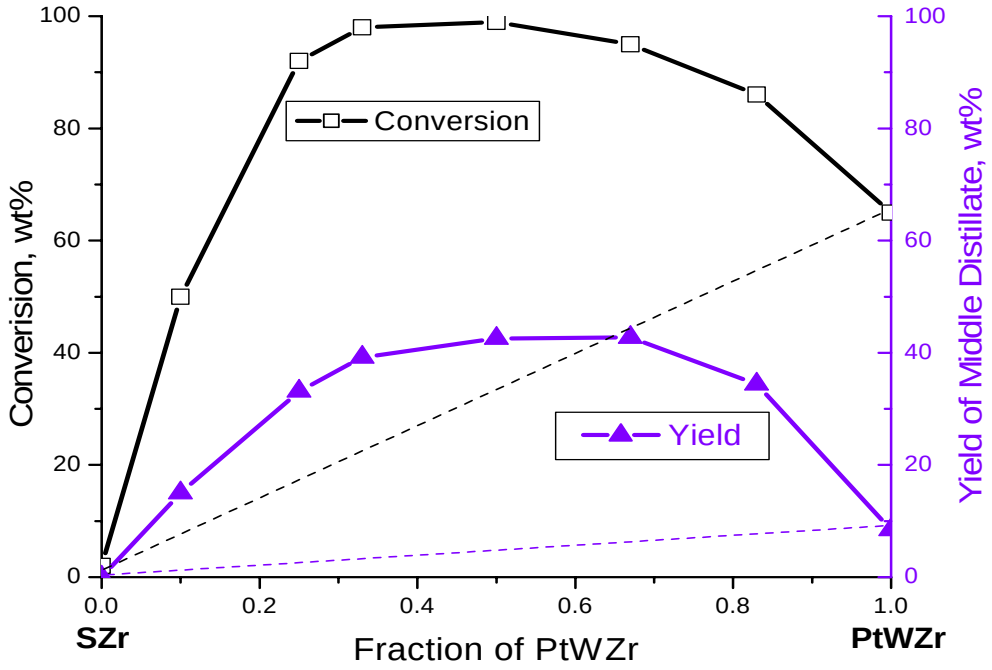

Catalyst: 0.2 g; Reactant: 0.8 g n-$C_{36}$ Reaction conditions: 200 °C, 25 min.

**Figure 40. Effect of Component Ratio on PtWZr/SZr Catalysts with 100-psi Hydrogen Pressure**

7.3.1.4 **Effect of Hydrogen Pressure on PtWZr/SZr Catalysts** Because hydrogen pressure can affect the performance of sulfated and tungstated zirconia catalysts in very different ways, it is an important factor for hybrid catalyst consisting of PtWZr and SZr components. The performance of PtWZr/SZr under higher hydrogen pressure (300 psi) is shown in Figure 41.

The PtWZr/SZr hybrid catalyst can maintain high reactivity and high yield to middle distillates over a larger range of component ratios when the hydrogen pressure is higher than the case shown in Figure 40. We have found that the reactivity of PtWZr decreases and the reactivity of PtSZr increases with higher hydrogen pressure. It shows that the SZr component is more sensitive to hydrogen pressure than is PtWZr in the hybrid system. In other words, when hydrogen pressure increases, the enhanced contribution of the SZr component exceeds the decrease of PtWZr activity. The performance of the whole PtWZr/SZr system is improved at a hydrogen pressure of 300 psi.

It should be noted that with higher hydrogen pressure, middle distillate yields do not always increase with conversion. The elevated cracking function of SZr in the PtWZr/SZr catalyst can lead to extended cracking which converts middle distillate fuels to gasoline products. As shown in Figure 41, PtWZr/SZr( 1:2) with 33 wt% PtWZr fraction has the highest reactivity, but its yield of middle distillate is lower than that of the PtWZr/SZr(3:1) catalyst ( with PtWZr fraction of 75 wt %).



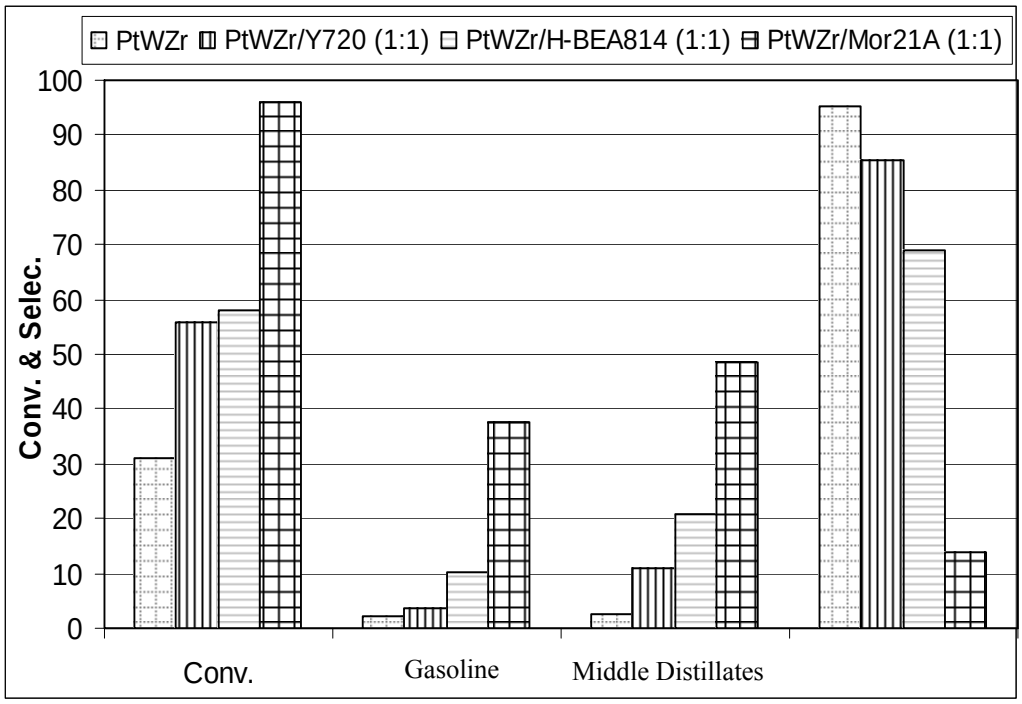

**Catalyst: 0.2 g; Reactant: 0.8 g n-$C_{36}$; Reaction conditions: 200 °C, 25 min.**

**Figure 41. Conversion of n-$C_{36}$ Using PtWZr/SZr Hybrid Catalysts with 300-psig Hydrogen Pressure**

### 7.3.2 Hybrid Catalysts Consisting of PtWZr and Zeolites

Zeolite catalysts are acidic materials that are commonly used in hydrocarbon conversions. Pt/zeolite catalysts usually require temperatures above 350°C. These high reaction temperatures tend to result in high selectivity to deeply cracked products of lower molecular weight than the middle range fuel products. To explore the use of zeolite material, we prepared hybrid catalysts by combining PtWZr with several zeolites as the second components. Dry-mixing preparation method was applied following the procedures in preparing PtWZr/SZr catalysts.

7.3.2.1 **Hybrid Catalysts with Various Zeolites** Different types of zeolite materials were added as a second component to PtWZr to form a hybrid catalyst. Since the acidity of a zeolite is related to its Si/Al ratio, we used zeolites with similar Si/Al ratios between 20 and 25. The zeolites we studied included mordenite (Mor21A), β-zeolite (BEA814) and Y zeolite (Y720). Detailed information for these samples is given in Table 3 of Chapter 4. The conversions and product distributions of PtWZr and the hybrid catalysts are shown in Figure 42.

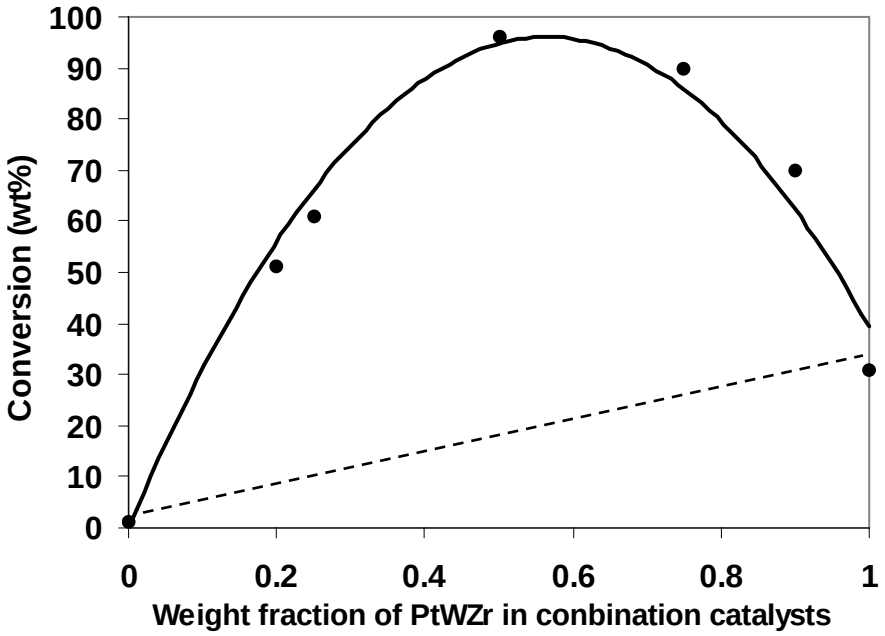



**Reaction conditions: 200 °C, *n*-$C_{36}$ /catalyst = 1.0 g/ 0.25g, 25 min., $H_2$ pressure = 500 psig**

**Figure 42. Conversion and Product Distribution Using PtWZr Combined with Y Zeolite, β Zeolite or Mordenite**

At 200°C, none of the zeolite catalysts alone have any detectable activity in converting n-$C_{36}$. However, all the 1:1 (weight ratio) hybrid catalysts were more active than the PtWZr catalyst. PtWZr/Mor (1:1) had the highest reactivity in converting *n*-$C_{36}$ and the highest selectivity to the middle distillates (48 wt %) and gasoline (37 wt %). Because it showed higher reactivities in converting n-$C_{36}$, further investigation of PtWZr/mordenite hybrid catalysts was carried out. Similar trends were observed for hybrid catalysts with other zeolites, but all with much lower reactivities than that of PtWZr/Mor.

7.3.2.2 **Effect of Component Ratio on PtWZr/mordenite** PtWZr/Mor(1:1) catalyst demonstrated higher activity than other PtWZr/zeolite hybrids for converting n-C36 to products in the desired transportation fuel ranges. In addition to 1:1 ratio, a series of catalysts with other ratios, varying from pure PtWZr (with 0.5 wt% Pt-loading) to pure Mor21A (without Pt-loading), were used in the tests of n-C36 conversion. The conversions of the different catalysts are shown in Figure 43. There are evident beneficial interactions between PtWZr and mordenite in the hybrid catalysts. If PtWZr and Mor21A act independently, the conversion curve would follow the straight line joining conversions of the pure components at the two ends of the x-axis. As in the case of PtWZr/SZr catalysts, there is a pronounced maximum conversion with a hybrid catalyst with about 55 wt % PtWZr.




**200 °C, *n*-$C_{36}$ /catalyst = 1.0 g/ 0.25g, 25 min, initial $H_2$ pressure = 300 psig**

**Figure 43. Conversion of n-$C_{36}$ using PtWZr/Mor Hybrid Catalysts with Different Component Ratios**

From the CO chemisorption results shown in Table 8 of Chapter 5, the PtWZr/Mordenite hybrid catalysts with a 1:1 wt component ratio had both higher Pt dispersion (61.8 %) and surface area (0.38 $m^2$/g.sample) than catalysts with other component ratios. This could be one of the reasons that the hybrid catalyst with a 1:1 ratio was more active.

# 8.0 CONCLUSIONS

Following are some conclusions from this research:

- The hydrocracking and hydroisomerization of long-chain normal paraffins, such as n-$C_{24}$ and n-$C_{36}$, can be effectively catalyzed using Pt-promoted tungstated zirconia (PtWZr) or Pt-promoted sulfated zirconia (PtSZr) catalysts to a range of products. PtWZr, a hydroisomerization catalyst, is a better candidate for producing middle distillate transportation fuels than is PtSZr, which is a strong cracking catalyst.

- Pt dispersion, an important factor related to catalyst reactivity, can be affected by Pt concentration. In the case of PtWZr, 0.25 wt% Pt gives a higher Pt dispersion and reactivity in n-$C_{24}$ conversion.

- The acidity (determined by TPD with ammonia) of anion-modified zirconia catalysts is related to their catalytic performance and can be affected by Pt loading, reduction with hydrogen and combination with a second component in a hybrid catalyst. While the 0.5 wt% Pt loading and reduction with hydrogen do not greatly affect the acidity of tungstated zirconia, they significantly change that of sulfated zirconia. The reduction with hydrogen at 400°C significantly decreases the acidity of PtSZr.

- Hybrid catalysts consisting of PtWZr and a second component, either SZr or a zeolite can lead to higher reactivities and yields to middle distillates than the individual

hybrid components. Both PtWZr and SZr contribute to the reactivity of the hybrid system. SZr alone can not maintain its reactivity without Pt loading. In a PtWZr/SZr hybrid catalyst, the PtWZr component helps to keep SZr from deactivation. The increased reactivity and selectivity to middle distillates of a PtWZr/SZr suggests active beneficial interactions between the components.

- Component ratios affect the reactivity and selectivity of a hybrid catalyst. For a given condition, there is an optimum component ratio for a maximum yield to desired products.

- Hydrogen pressure affects the performance of PtWZr and of PtSZr catalyst differently in the hydrocracking and hydroisomerization of long-chain paraffins. Higher hydrogen pressure (>100psi) increases PtSZr reactivity while it decreases the reactivity of PtWZr. The opposite effects of hydrogen pressure on the two types of zirconia catalysts make it an important factor for changing the balance of the component functions in a PtWZr/SZr hybrid catalyst.

- Evidence from characterization tests (SEM, XRD, BET and TPD) showed that the hybrid catalysts prepared in this research are mechanical mixtures of the two types of components.

- Mordenite, Y and beta zeolite with similar Si/Al ratio can also be used as a second component to form PtWZr/zeolite hybrid catalysts with improved performance. The performance of the hybrid catalysts are affected by zeolite type and component ratio.

In this work, we investigated the application of the special properties of anion-modified zirconia in the conversion of long-chain alkanes in FT wax into middle distillate fuels such as

diesel. In addition to the use of pure PtWZr and PtSZr catalysts, we explored the combination of PtWZr and WZr to form a hybrid catalyst and obtained active and beneficial interactions between the hybrid components. Many characterization tests have been carried out in an endeavor to understand the novel hybrid catalyst systems. PtWZr/zeolite hybrid catalysts were also studied in a similar way, using zeolites as the second hybrid catalyst for catalyst systems for improved yield of middle distillates. The application of PtWZr/zeolite hybrid systems confirms that an active hybrid system can be prepared using various components.

This research demonstrates a better utilization of anion-modified zirconia via using hybrid catalysts for production of middle distillates. We tested and compared various catalyst systems with an established set of reaction conditions (200°C reaction temperature, 25 minutes reaction time and 4:1 reactant/catalyst ratio). All the reaction conditions as well as other variables can be used as a way to fully exploit the high potential and flexibility of the promising application of hybrid catalysts. For example, as shown in Table 16, at a higher temperature, 210°C, and 350 psi hydrogen pressure, yield to middle distillates as high as 70 wt% can be achieved using PtWZr/SZr(3:1) in 30 minutes. With this work, we hope to furnish a foundation for further investigations.

# 9.0 FUTURE WORK

Interesting and promising hybrid catalysts consisting of anion-modified zirconia catalysts have been successfully prepared and applied in conversion of long-chain hydrocarbons in FT waxes into desired middle distillates. In this research, the various catalysts were evaluated and compared using an established set of reaction conditions. To fully investigate the application of these catalysts, other reaction conditions, such as reaction temperature, reaction time and catalyst/reactant ratio have to be studied to further understand the catalysts and to achieve their highest potential.

In addition to the model compounds, n-$C_{24}$ and n-$C_{36}$, more experiments should be carried out with the various real FT waxes already at our disposal.

Research should be extended to determine the effect of impurities in an FT wax on the performance of the catalysts.

In the preparation of hybrid catalyst systems, the catalyst components and preparation methods we studied are limited. WZr or SZr with different amounts of tungstate or sulfated species have been obtained and should be tested as components of the hybrid catalysts.

A Pt/amorphous silica-alumina catalyst with Si/Al ratio of 100 has been reported to convert long-chain alkanes to middle distillate in high yield[5, 141]. It is desirable to obtain amorphous silica-alumina sample with high Si/Al ratio and study its performance in our systems.

Measure and compare acidities and catalytic reactivities of these materials for a better understanding of these catalysts.

Promoters other than Pt, such as Pd, can be used to study its effect on the balance of hydroisomerization and hydrocracking.

While the "Dry-mixing" method gives active hybrid catalysts, other techniques might help to enhance catalyst performance. Use of a ball mill[124] for grinding the various components of a hybrid catalyst should be studied.

This work has been carried out using a batch reactor system. The catalysts should be tested in a continuous reaction system with on-line sampling. To avoid blockage problems, a solvent should be used.

# APPENDIX A

# REACTION RESULTS

**Table 15. Reaction Results with n-$C_{24}$ as Reactant**

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **R80** | PtWZr, In-House[a] | 300 | 200 | 25 | 46 | 3 | 7 | 90 |
| **R85** | PtSZr, 1:12[b] | 300 | 200 | 25 | 61 | 82 | 10 | 8 |
| **RM155** | WZr | 500 | 200 | 25 | 1 | 0 | 38 | 62 |
| **RM153** | SZr | 500 | 200 | 25 | 1 | 53 | 29 | 18 |
| **R88** | PtWZr | 300 | 200 | 25 | 48 | 2 | 9 | 89 |
| **R127** | PtWZr | 500 | 200 | 20 | 29 | 2 | 3 | 95 |
| **RM125** | PtWZr | 500 | 200 | 25 | 41 | 4 | 3 | 93 |
| **RM119** | PtWZr | 500 | 200 | 25 | 33 | 2 | 2 | 96 |
| **R077-2** | PtWZr | 500 | 210 | 25 | 73 | 7 | 25 | 68 |
| **RM077** | PtWZr | 500 | 230 | 25 | 95 | 15 | 41 | 44 |

Table 15 (Continued)

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **RM158** | 0.25%[c] Pt, PtWZr | 500 | 200 | 20 | 50 | 2 | 7 | 91 |
| **R424** | 1.0[c] PtWZr | 500 | 200 | 25 | 26 | 0 | 2 | 98 |
| **R78** | PtSZr, In-House[a], 1:12[b] | 300 | 200 | 25 | 62 | 85 | 9 | 6 |
| **R351** | PtSZr | 300 | 200 | 20 | 90 | 85 | 12 | 3 |
| **R149** | PtSZr | 500 | 200 | 20 | 98 | 90 | 10 | 0 |
| **RM151** | PtSZr, 1:12 | 500 | 200 | 15 | 33 | 80 | 8 | 12 |
| **RM159** | PtWZr/WZr(1:1) | 500 | 200 | 20 | 68 | 14 | 30 | 56 |

a. Except addressed specifically, catalysts are prepared using MEI samples
b. Except addressed specifically, the catalyst/reactant weight ratio is 1:4
c. Except addressed specifically, the Pt-loading is 0.5 wt%

**Table 16. Reaction Results with n-$C_{36}$ as Reactant**

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **RM223** | 0.25%[a] Pt PtWZr | 500 | 200 | 25 | 64 | 6 | 18 | 76 |
| **R224** | 1.0%[a] Pt PtWZr | 500 | 200 | 25 | 35 | 5 | 8 | 87 |
| **R194** | PtWZr | 500 | 200 | 25 | 52 | 6 | 10 | 84 |
| **R194-1** | PtWZr | 500 | 200 | 35 | 72 | 9 | 36 | 55 |
| **R194-2** | PtWZr | 500 | 220 | 25 | 89 | 13 | 34 | 53 |
| **RM193** | PtWZr | 500 | 200 | 25 | 40 | 0 | 2 | 98 |
| **RM201** | PtWZr | 300 | 200 | 25 | 92 | 4 | 16 | 80 |
| **RM225** | PtWZr | 100 | 200 | 25 | 95 | 9 | 41 | 50 |
| **RM226** | PtWZr | 50 | 200 | 25 | 97 | 11 | 40 | 49 |
| **RM227** | PtWZr | 20 | 200 | 25 | 94 | 10 | 30 | 60 |
| **RM231** | PtWZr | 10 | 200 | 25 | 80 | 8 | 25 | 67 |
| **RM232** | PtWZr | 5 | 200 | 25 | 76 | 6 | 18 | 76 |

Table 16 (Continued)

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **RM272** | PtSZr | 100 | 200 | 20 | 45 | 10 | 27 | 63 |
| **R272-2** | PtSZr | 100 | 200 | 25 | 58 | 31 | 26 | 43 |
| **R272-4** | PtSZr | 100 | 210 | 20 | 78 | 59 | 20 | 21 |
| **RM265** | PtSZr | 300 | 200 | 20 | 60 | 34 | 42 | 24 |
| **RM266** | PtSZr | 400 | 200 | 20 | 84 | 50 | 30 | 20 |
| **R245** | PtSZr | 500 | 200 | 20 | 95 | 65 | 20 | 15 |
| **R464** | PtWZr/SZr (1:1), Direct Addition[b] | 300 | 200 | 25 | 30 | 3 | 12 | 85 |
| **R164** | PtWZr/SZr (1:1), WetMix[b] | 300 | 200 | 25 | 26 | 2 | 7 | 91 |
| **R362** | PtWZr/SZr (1:1) | 300 | 200 | 25 | 93 | 18 | 45 | 37 |
| **R384** | PtWZr/PtSZr(1:1) | 300 | 200 | 25 | 95 | 88 | 8 | 4 |
| **R401** | PtWZr/SZr(1:2), 0.2g[c] | 100 | 200 | 25 | 44 | 6 | 25 | 69 |
| **R276** | PtWZr/SZr(1:1), 0.2g[c] | 100 | 200 | 20 | 55 | 9 | 24 | 67 |

Table 16 (Continued)

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **RM277** | PtWZr/SZr(1:1), 0.2g | 100 | 200 | 25 | 67 | 14 | 32 | 54 |
| **R277-2** | PtWZr/SZr(1:1), 0.2g | 200 | 200 | 25 | 75 | 19 | 45 | 36 |
| **R403** | PtWZr/SZr(2:1), 0.2g | 100 | 200 | 25 | 82 | 18 | 48 | 34 |
| **RM291** | PtWZr/SZr(3:1), 0.2g | 100 | 200 | 25 | 90 | 15 | 53 | 32 |
| **R318** | PtWZr/SZr(3:1), 0.2g | 300 | 200 | 25 | 93 | 18 | 60 | 22 |
| **R319** | PtWZr/SZr(3:1), 0.2g | 350 | 210 | 30 | 95 | 20 | 74 | 6 |
| **R402** | PtWZr/SZr(5:1), 0.2g | 100 | 200 | 25 | 91 | 13 | 43 | 44 |
| **RM258** | PtWZr, 0.2g | 100 | 200 | 25 | 86 | 5 | 24 | 71 |
| **RM413** | PtWZr/SZr(1:3), 0.2g | 300 | 200 | 25 | 92 | 59 | 36 | 5 |
| **RM415** | PtWZr/SZr(1:2), 0.2g | 300 | 200 | 25 | 98 | 55 | 40 | 5 |
| **RM286** | PtWZr/SZr(1:1), 0.2g | 300 | 200 | 25 | 93 | 45 | 43 | 12 |
| **RM418** | PtWZr/SZr(2:1), 0.2g | 300 | 200 | 25 | 95 | 34 | 45 | 21 |

Table 16 (Continued)

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | |
|---|---|---|---|---|---|---|---|---|
| | | $P^{i}_{H2}$, psi | T, °C | Time, min | Conversion | Gasoline | Middle Distillates | Lube-base Oil |
| **RM419** | PtWZr/SZr(5:1), 0.2g | 300 | 200 | 25 | 86 | 25 | 40 | 35 |
| **RM421** | PtWZr | 300 | 200 | 25 | 65 | 5 | 13 | 82 |
| **R146** | PtWZr/Mor(1:4) | 300 | 200 | 25 | 51 | 18 | 35 | 47 |
| **R346** | PtWZr/Mor(1:2) | 300 | 200 | 25 | 60 | 25 | 36 | 49 |
| **RM221** | PtWZr/Mor(1:1) | 300 | 200 | 25 | 94 | 35 | 40 | 25 |
| **R221-1** | PtWZr/Mor(1:1) | 300 | 220 | 25 | 98 | 53 | 36 | 11 |
| **R221-3** | PtWZr/Mor(1:1) | 300 | 200 | 30 | 96 | 45 | 39 | 16 |
| **R347** | PtWZr/Mor(3:1) | 300 | 200 | 25 | 90 | 6 | 32 | 62 |

a. Except addressed specifically, the Pt-loading is 0.5 wt%
b. Except addressed specifically, the hybrid catalysts are prepared via “Dry-mixing” method
c. Except addressed specifically, 0.25g catalyst is used in each run and the catalyst/reactant ratio is 1:4

**Table 17. Data for Figure 11: Effect of Pt Concentration on Pt Dispersion and Pt Surface Area over Tungstated Zirconia**

| Pt Concentration, wt % | Pt Dispersion, % | Pt Surface area, $m^2$/g.WZrSample |
|---|---|---|
| **0.25** | 72.5 | 0.45 |
| **0.5** | 58.8 | 0.73 |
| **0.75** | 36 | 0.43 |
| **1.0** | 3.1 | 0.08 |

# APPENDIX B

## SIMULATED DISTILLATION OF PRODUCTS FROM FISCHER-TROPSCH WAXES

The products obtained from Fischer-Tropsch waxes can be analyzed by simulated distillation to determine their boiling point characteristics. Simulated distillation is based on the observation that some GC columns, such as an HP-crosslinked methylsilicone column) release hydrocarbons in the order of their boiling points, simulating a physical distillation. The area under the chromatogram is measured as a function of time during the column temperature is increased at a programmed rate. The area axis is normalized to 100% to obtain the percent of sample recovered at a given time. The time axis is converted to boiling point using a calibration curve obtained by analyzing a mixture of n-alkanes of known boiling points under identical conditions. Since the products from Fischer-Tropsch (FT) waxes over anion-modified zirconia catalysts are mainly isoalkanes and n-alkanes, simulated distillation is a useful technique for determining their distillation ranges.

A FT wax sample, EI-CIS21, was obtained from Energy International (EI). The hydrocarbons of different carbon number are shown in Figure 44 using a simulated distillation column. We used a standard sample as a marker to identify the peaks. The EI-CIS has an average carbon number of about $C_{21}$ and the heaviest component is $C_{50}$+. The simulated distillation of

EI-CIS21 wax is shown in Figure 45. According to the range of boiling point, the gasoline distillate (less than 200 °C) in the wax is less than 5 wt% and the middle distillates about 40 wt %.

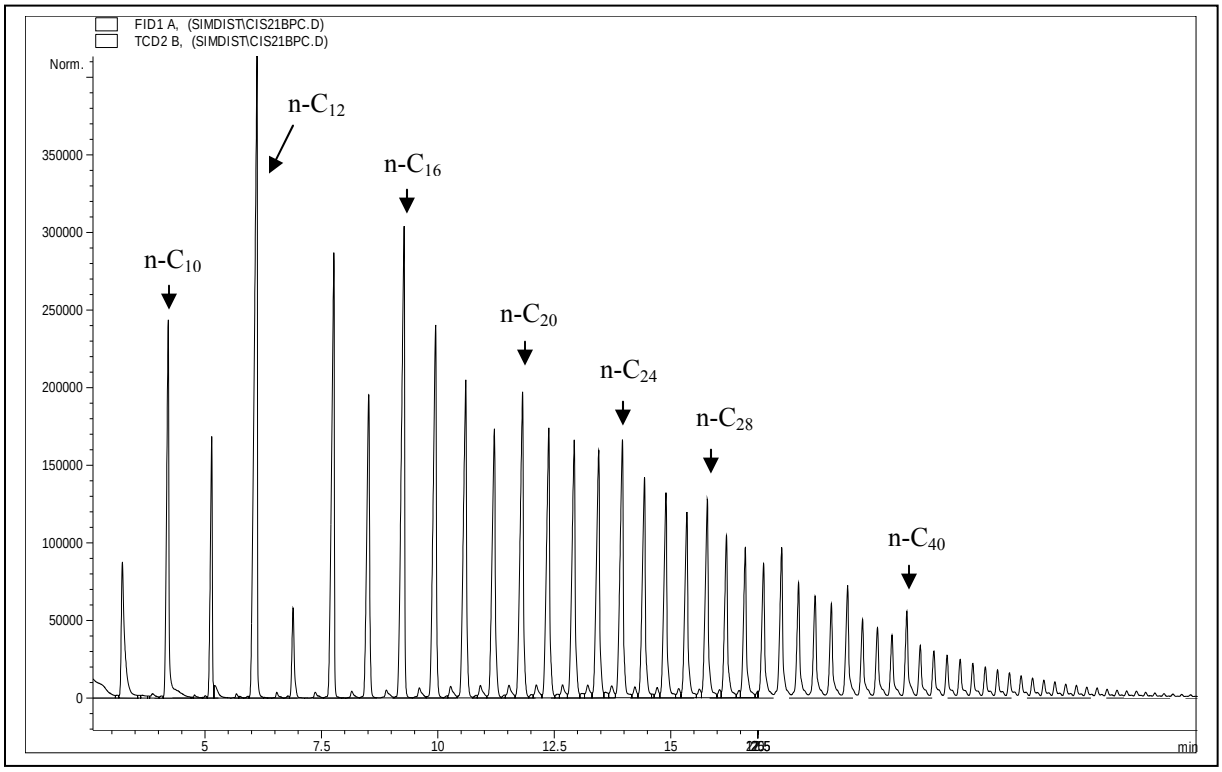



**Figure 44. Composition of EI-CIS21 Wax**

The EI-CIS21 wax was treated with PtWZr/SZr (1:1) catalyst (0.25g catalyst,1.0 g wax, 200 °C, 300psi hydrogen pressure and 25 minutes). The products composition after the treatment is shown in Figure 46. Compared with the original wax, the gasoline distillate increased from about 5 wt% to 45 wt% and there are about 45 wt % middle distillates in the products.

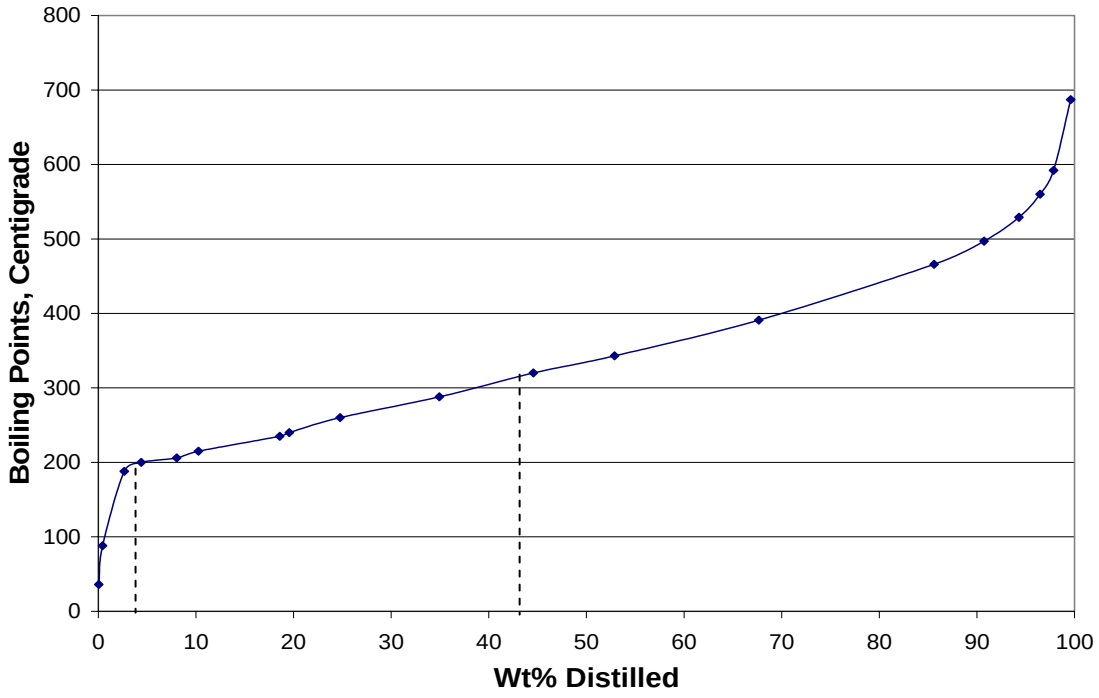



**Figure 45. Simulated Distillation of EI-CIS21 Wax**

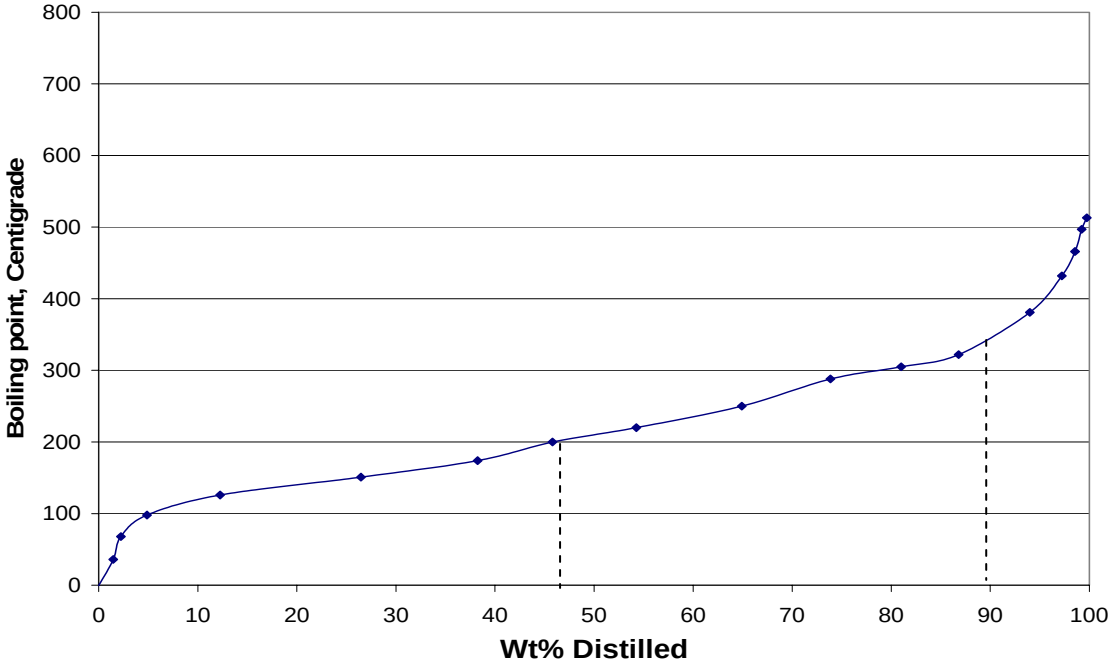



**Figure 46. Simulated Distillation of Liquid Products from EI-CIS21 Wax**

# APPENDIX C

## PRELIMINARY KINETIC CALCULATIONS

Because of the limitation of a batch reactor system, we did not carry out further kinetic study on the reaction processes with various catalyst systems. In a preliminary study, we calculated the ratio of cracking rate to isomerization rate (A) for some catalysts as an effort to evaluate the effect of the relative strength of cracking and isomerization functions on their catalytic characteristics.

For a normal hydrocarbon (Cn) with carbon number of n, assume it goes through two types of reactions during the conversion, as

Isomerization of Cn, $Cn \rightarrow Ci$ (1) and

Cracking of Ci, $Ci \rightarrow Cc$ (2)

From (1), $dCn/dt = -r_i \times Cn$ (3) $r_i$ is the rate of isomerization

From (2), $dCi/dt = r_i \times Cn - r_c \times Ci$ (4) $r_c$ is the rate of cracking

(4)/(3), $dCi/dCn = -1 + (r_c / r_i) \times Ci /Cn$

Define $A = r_c / r_i$, and let $u = Ci /Cn$,

Then, $u + Cn \times du/dCn = -1 + A \times u$

$d \ln[ u \times (A-1)] = d \ln Cn^{A-1}$

At $t = 0$, $Cn = 1$; At $t = t$, $Cn = Cn$

Therefore, $\ln \{[u \times (A-1)-1]/(-1)\} = \ln (Cn^{A-1})$

$$1+ (1-A) \times Ci/Cn = Cn^{A-1} \qquad (5)$$

For a given Ci and Cn, the value of A can be solved using equation (5).

We used MathCAD Professional to calculate the values of A of various catalysts in converting long-chain alkanes. To compare the A-values of different catalysts, experiment data with same reactant, same reaction temperatures and close conversion were used.

For example, in the conversion of n-$C_{36}$ as shown Table 18, PtWZr has an A value of 0.30 and the A value of PtWZr/SZr (1:1) is 1.48. The low cracking/isomerization rate ratio of PtWZr shows that it has more isomerization function than cracking function, so that the major products are the isomers of the reactant. With a higher A-value, PtWZr/SZr hybrid catalyst has much stronger cracking function that is necessary for higher yield of middle distillates.

**Table 18. Cracking/isomerization Ratio (A) of PtWZr and PtWZr/SZr(1:1) in n-$C_{36}$ Conversion**

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | | A |
|---|---|---|---|---|---|---|---|---|---|
| | | $P^i_{H2}$, psi | T, °C | Time, min | Conv. | Gasoline | Middle Distillates | iso-$C_{36}$ | |
| **RM258** | PtWZr | 100 | 200 | 25 | 85 | 5 | 23 | 70 | 0.30 |
| **R 280** | PtWZr/SZr (1:1) | 100 | 200 | 15 | 82 | 21 | 39 | 25 | 1.48 |

Table 19 shows the difference of A-values of PtWZr and PtSZr catalysts. PtSZr has the high A-value of 3.84, suggesting a cracking function much stronger than the isomerization functions. In the products using PtSZr, there is more gasoline than isomers of n-$C_{36}$. For the PtWZr catalyst, the rate of cracking reactions is less than that of isomerization reactions, so that the A-value is less than 1. We noticed that PtWZr has different A-values with different conversions. The comparison of A-values should be carried out using experiment results with close conversions.

**Table 19. Cracking/isomerization Ratio (A) of PtWZr and PtSZr in n-$C_{36}$ Conversion**

| Run Number | Catalyst | Reaction Conditions | | | Results, wt% | | | | A |
|---|---|---|---|---|---|---|---|---|---|
| | | $P^i_{H2}$, psi | T, °C | Time, min | Conv. | Gasoline | Middle Distillates | iso-$C_{36}$ | |
| **R 232** | PtWZr | 300 | 200 | 15 | 58 | 4 | 9 | 54 | 0.71 |
| **RM265** | PtSZr | 300 | 200 | 10 | 60 | 36 | 40 | 22 | 3.84 |

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